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Correlating wettability alteration with changes in gas permeability in gas condensate reservoirs

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Correlating wettability alteration with changes in gas permeability in gas condensate reservoirs

by

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Dedication

To my family

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Abstract

Correlating wettability alteration with changes in gas permeability in gas condensate reservoirs

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Altering the wettability of reservoir rock using fluoro-chemical treatments has proved to be a viable solution to the condensate blocking problem in gas wells. Alteration of rock wettability to neutral-wet is the primary reason for improvement in gas and condensate relative permeabilities. Stability/compatibility test, drop tests and X-ray photoelectron spectroscopy (XPS) analysis along with core flood results were used to characterize wettability changes.

XPS tests, drop tests, and relative permeability measurements were conducted and correlated with each other. It is shown that XPS analysis and imbibition tests provide a quantitative measure of chemical adsorption and surface modification, but only a qualitative measure of the possible change in relative permeability. As such these simple analytical tools may be used as a screening tool. A positive but imperfect empirical

correlation was obtained with results from core flood experiments. The varying concentration of fluorine observed on the rock surface was found to be directly correlated to the wettability change in the rock, which in turn is responsible for improving the deliverability of wells in gas condensate/volatile oil reservoirs.

The method discussed in this thesis can be used to identify chemical treatments to change rock wettability and, therefore, relative permeability. This provides a simple, quick and inexpensive way to screen chemicals as wettability altering agents and relative permeability modifiers which saves time, cost and effort.

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CHAPTER 1: INTRODUCTION

A typical problem associated with gas condensate wells operating below the dew point is that of condensate blocking. As the pressure near the well drops below the dew point, condensate (liquid) begins to from. The condensed liquid is trapped by capillary forces which results in build up of a liquid phase in the formation around the wellbore. This build up leads to a decrease in the effective permeability to gas which can significantly decrease gas production.

Over the years, researchers have proposed several methods to restore gas production rates after a decline due to condensate blocking. Gas injection, hydraulic fracturing, horizontal wells and methanol injection have all been tried but these methods either offer only temporary productivity improvement or are only applicable in specific situations. However, altering the wettability of reservoir rock using fluorochemical treatments has proved to be a viable solution to the condensate blocking problem in gas condensate wells as shown by field trials[1]. Altering the wettability of porous media from strongly water-wet or oil-wet to intermediate-wet reduces the residual liquid saturations and results in an increase in the relative permeability to gas resulting in an increases in the gas production rate.

The following sequential procedure was employed in order to select the treatment solution. As a first step, screening tests were conducted to better understand and identify the chemical treatments that would be used for wettability alteration. These tests included stability tests/compatibility tests, drop tests and X-ray electron spectroscopy (XPS) analysis. The results from these tests were used in conjunction with the core flood experiments that were conducted under reservoir conditions to measure the effect of wettability change and the improvement from it. The results showed that XPS analysis

and drop tests provide a quantitative measure of chemical adsorption and surface modification but only a qualitative measure of the possible change in relative permeability. A positive but imperfect empirical correlation was obtained when comparing the screening test results with corefloods. The varying concentration of fluorine observed on the rock surface was found to be positively correlated with the wettability change in the rock which in turn is responsible for improving the deliverability of wells in gas condensate reservoirs. This provides a simple and inexpensive way to screen chemicals as wettability altering agents and relative permeability modifiers which saves time, cost and effort.

1.1 RESEARCH OBJECTIVES

The objective of this research is to develop a methodology for selecting chemical treatments that have the potential to be used for reducing the damage from condensate blocking. The specific objectives can be summarized as follows

- Identify and screen chemical treatments/fluoro surfactants that are capable of altering the wettability of reservoir rocks from water-wet to neutral-wet and thereby improving the gas and condensate relative permeability
- Investigate the relationship between surface fluorine concentration, wettability change and improvement in relative permeability after treatment. This would be achieved with results from core flood experiments, X-ray photo electron spectroscopy analysis and drop tests on treated cores.

CHAPTER 2: LITERATURE REVIEW

2.1 GAS CONDENSATE RESERVOIRS

Reservoirs bearing gas-condensates are becoming more common as the petroleum industry goes to greater depths to explore for oil and gas. Accuracy in engineering computations for gas-condensate systems (e.g., well testing, estimating reserves, sizing surface facilities, and predicting productivity trends) depends upon a basic understanding of phase and flow behavior relationships. When we compare dry- gas reservoirs with gas-condensate reservoirs, there are many factors which affect the performance of gas-condensate reservoir during the exploitation process that need to be understood[2].

The fluid initially exists as a gas, but as the reservoir pressure declines below the dew point of the fluid, a liquid rich phase starts to drop out of the gas phase. This liquid rich phase is termed “condensate” and the phenomenon is called “condensate banking”. Since the largest pressure drop occurs near the producing wells, the formation of condensate phase usually occurs as a near well bore phenomenon. As the pressure decreases, the liquid continues to accumulate occupying the rock pores that otherwise would be available for gas flow, leading to a decrease in the effective permeability to gas. Another disadvantage is that the produced gas contains fewer valuable heavy end hydrocarbons because these dropout throughout the reservoir, where the condensate has insufficient mobility to be produced to the surface. Figure 2.1 shows the phase diagram for a gas condensate reservoir.

Theoretically, flow in gas-condensate reservoirs can be divided into three reservoir regions, though they might not all always be present. The two regions closest to a well can exist when bottom-hole pressure goes below the dew point of the fluid. The

third region, away from producing wells, exists only when the reservoir pressure is above the dew point.

Region 1: This is the near-well bore region characterized by the steady state flow of gas and condensate. It has condensate saturation at or above critical saturation. In this region, high flow rate conditions prevail.

Region 2: This region is characterized by pressure slightly below the dew point pressure, low condensate saturation, low interfacial tension and high gas velocity. At these low saturations, condensate remains immobile and the only fluid that flows is gas.

Region 3: An outer region containing single-phase gas. Average reservoir pressure is above the dew point pressure. Gas velocity is low in this region. Figure 2.2 shows the three regions.

There may also exist a region immediately near the well-bore region where high trapping (capillary) number leads to decreased condensate saturation and increased gas mobility through "velocity stripping" [3].

In some cases, however, this might not be a near well-bore phenomenon. It is due to the fact that the average reservoir pressure might be below the dew point pressure, which results in dropout of condensate throughout the reservoir. The amount of liquid phase present depends not only on pressure and temperature, but also on the composition of the fluid. A dry gas, theoretically, does not have sufficient heavy end hydrocarbons to cause significant liquid drop out. A lean gas condensate generates a small volume of the liquid phase, less than 10 STB/MMSCF (0.75% by volume) and a rich gas condensate generates a larger volume of liquid, generally more that 150 STB/MMSCF (11.4% by volume). There are no strict definitions of lean or rich condensate fluids and the above mentioned values are only provided as examples.

2.2 PRODUCTIVITY DECLINE IN GAS CONDENSATE RESERVOIRS

Engineer[4]studied Cal Canal Field in California, which produced a very rich gas condensate fluid and had a very high water saturation of 59%. The total gas recovery expected from the Cal Canal Field was as low as 10% because of high condensate and water saturation in the near well-bore region.

Cvetkovic et al.[5] studied production from rich gas condensate reservoirs. They concluded from their radial simulation studies that composition of a gas condensate can significantly affect the relative permeability to gas. They claimed that the condensate problem is not significant for lean gas. Their results contradict the significant production loss reported in the lean gas condensate fields like Arun and North Sea.

Well productivity in the Arun field, Indonesia, declined significantly after producing for 10 years. Afidick et al.[6] studied this decline and concluded that this loss in productivity is due to condensate accumulation. Experimental PVT analysis of the reservoir fluid showed that the reservoir fluid was a lean gas condensate with maximum liquid dropout of 1.1% as a result of which productivity declined by a factor of around 2.

Barnum[7] reported two wells that died due to condensate blockage. The author reported a decrease in productivity by a factor up to five due to condensate accumulation near the well-bore.

Shell and Petroleum Development Oman reported a 67% productivity loss for wells in two fields[8]. Chevron reported a loss of productivity for some of the wells in a gas condensate field in the North Sea[9]. Other large gas-condensate resources which have reported significant reduction in productivity due to condensate blocking include Shtokmanovskoye field in the Russian Barents Sea, Karachaganak field in Kazakhstan,

the North field in Qatar that becomes the South Pars field in Iran, and the Cupiagua field in Colombia[10].

Anderson et al.[11] reported a reversal in productivity decline. The productivity of wells in this moderate rich gas condensate reservoir declined quickly as the bottom-hole pressure dropped below the dew point. By virtue of compositional modeling, the condensate saturation was reported at 68%, thus causing the observed decline in productivity. However, at the point when the pressure through out the reservoir dropped below the dew point, the gas productivity began to increase. The reason for this phenomenon was that the gas now moving towards the well-bore was leaner and had less condensate to drop out in the near well-bore area. This was confirmed with modeling results that showed the condensate saturation to be at 55% resulting in decreased condensate blockage and increased gas permeability.

2.3 STUDIES ON RELATIVE PERMEABILITY

As shown in Figure 2.2 Region 1, the flow process in the near well-bore region (where condensate banking has the most impact) becomes a steady-state flow process and thus the relative permeability data should be measured with a steady-state method. As the change in relative permeability is a major source of concern for these reservoirs, it has been investigated and well-documented over the years.

One of the earliest laboratory experiments on gas condensate fluids was done by Ham et al.[12] Nitrogen and condensate fluid from a reservoir were used in the experiment. The effects of liquid-vapor volume ratio relationship, condensate saturation, pressure, apparent velocity, fluid composition and core type on the mobility of gas were examined. It was concluded that relative mobility and liquid-vapor volume ratio relationships are dependent on pressure, saturation and velocity.

Hinchman et al.[13] used a compositional one-dimensional radial model to predict the performance of a gas condensate well. The effect of composition (fluid properties, liquid dropout rate) and gas-oil relative permeability on gas productivity were investigated. Their results showed that relative permeability data is the most sensitive parameter in determining productivity loss. They also proposed that the amount of gas-condensate banking is dependent on the richness of the gas-condensate and the liquid viscosity.

Gravier et al.[14] studied a carbonate gas field to determine gas and condensate relative permeabilities using a ternary pseudo-reservoir fluid of methane/pentane/nonane. Their results confirmed the damage due to condensate banking that the gas relative permeability decreased from an average value of 0.68 to about 0.10 as the condensate saturation increased from 0 to 30%.

Sognesand[15] studied the condensate banking in vertically fractured gas-condensate wells. The effects of fluid properties and relative permeabilities were considered, as is the effect of production mode - i.e. constant-rate versus constant-sandface-pressure production. He concluded that constant pressure production results in maximum condensate buildup near fractures.

Henderson et al.[16] measured steady state relative permeabilities for gas condensate fluids and found that relative permeabilities of both gas and condensate phases are rate sensitive and increase with velocity. These experiments were performed over a wide range of CGR (condensate to gas ratio), IFT (interfacial tension) and velocities. They also concluded that relative permeabilities of both gas and condensate phases increased as IFT was lowered.

Relative permeability measurements for two North Sea gas condensate fluids were performed by Chen et al.[17]. The authors used recombined fluids from two North Sea

gas condensate reservoirs and 29' composite cores for their study. Their results showed that critical condensate saturation and relative permeability are sensitive to flow rate and interfacial tension and high interfacial tension caused the decrease in condensate relative permeability as condensate saturation increased. Experimental work performed at The University of Texas at Austin by Du et al.[18], Walker et al.[19] and Al-Anazi et al.[20] showed that condensate dropout reduced the gas relative permeability by an order of magnitude. They further noted that the reduction in relative permeability is more severe in the presence of high water saturation. The experiments were done on high and low permeability rocks and the decline observed in normalized PI (ratio of PI during two phase flow to PI during single phase flow i.e. ratio of damaged PI to original PI) was almost the same.

Similar core flood experiments were performed by Ayyalasomayajula et al. [21] and focused on the effect of capillary number for several different reservoir rocks for a wide range of k_{rg}/k_{ro} values. The authors reported major improvement in gas relative permeability with increasing capillary number for all the rock types studied. Further work on permeability as a function of capillary number and k_{rg}/k_{ro} ratio was done by Kumar et al.[22] when he measured gas and condensate relative permeabilities on both sandstone and limestone rocks over a wide range of conditions, capillary numbers and fluid types. The author reported a significant increase in gas relative permeability for capillary numbers greater than 10^{-4}. The author however neglected the effects of non-Darcy flow, which can be significant at the high flow rates used to achieve high capillary numbers.

2.4 METHODS TO TREAT CONDENSATE BANKING

Various methods have been proposed, investigated and implemented to remove the damage caused by condensate blocking.

Abel et al.[23] proposed that gas cycling can serve as a possible mechanism to treat the damage due to condensate banking. He proposed the following two schemes for gas cycling.

- Full pressure maintenance: In this case, condensate is kept on production as gas is injected continuously into the reservoir. This prevents the reservoir pressure from dropping below the dew point.
- Partial pressure maintenance: In this case, gas injection commences only after the reservoir pressure drops below the dew point. This is done in order to slow down the pressure decline and re-vaporize or displace the condensate through miscible process.

Similar to Abel's work, Luo et al.[24] performed experiments on rich gas condensate fluids. His experiments were based on full pressure and partial pressure maintenance schemes with injection of lean gas. The observed results confirmed that the heavier components get vaporized and can be recovered when gas is injected above saturation pressure as compared to when gas is injected below the saturation pressure.

Marokane et al.[25] also observed and studied the effect of injecting produced gas for condensate removal. His results were based not only on lean gas fluids but also included gas condensate fluids. For lean gas condensate type fluids, he proposed that produced gas should be injected only after reservoir pressure drops below the maximum liquid drop out pressure. However for rich gas condensate, he suggested that gas injection is more efficient when produced gas is injected at a pressure greater than the maximum liquid dropout pressure.

Fishlock et al.[26] observed the effect of water injection for mitigating the condensate banking damage. He did his experiments on lean and rich gas condensate systems and concluded that leaner fluids provide higher recoveries. He said that the reason behind this phenomenon was the presence of a higher proportion of oil in the gas phase at a given pressure in a lean fluid as compared to a rich fluid.

Ahmed et al.[27] compared water injection with gas injection schemes for mitigating condensate blocking problems. He concluded that both processes improve the recovery but gas injection may not be economical because of higher initial investment, higher operating cost and delay in gas sales.

Kossack et al.[28] performed simulations to observe the condensate removal process through injection of multiple slugs of gas for both homogeneous and heterogeneous reservoirs. Here, a slug of methane was injected followed by nitrogen. His results showed that additional recovery is achieved if his proposed methodology of injection is used.

Sanger et al.[29] studied the effectiveness of condensate removed with the use of methane and nitrogen slugs. He observed that the evaporation capacity of methane is 20 times higher than that of nitrogen. He also reported that a disadvantage of injecting nitrogen is that the dew point of the mixture is higher than reservoir gas. This causes the condensate to drop out due to mixing with gas condensates in the reservoir itself.

Jamaluddin et al.[30] observed the effect of CO_2 and Propane on phase behavior of gas condensate fluids. He proposed the use of methane in "Huff and Puff" injection for mitigating condensate banking as it reduces both the dew point and total liquid dropout. He also reported that using CO_2 would reduce the total liquid drop out but increase the dew point of the mixture.

Ahmed et al.[31] analyzed the effectiveness of lean gas, nitrogen and carbon dioxide in a "Huff and Puff" injection manner for condensate removal. This technique involves

using the same well alternatively acting as a producer and an injector. The author proposed that Huff and Puff injection was most productive when done before the maximum liquid drop out is reached. He also proposed that when injecting at the same pressure, CO2 performs the best of the tested gases.

Cullick et al.[32] performed some simulation and experimental work on the effectiveness of water alternating gas (WAG) for improving deliverability in condensate reservoirs. He concluded that WAG is better than dry gas injection in full pressure maintenance process and showed an improvement of 28% to 54% in this manner as compared to continuous injection with full pressure maintenance.

Henderson et al.[33] studied the effect of water injection on gas condensate recovery by performing core floods. He performed the core floods both above and below dew point and concluded that the residual hydrocarbon saturation after water flooding depends primarily on the interfacial tension between the gas and condensate. He suggested that an optimum water injection period exists during which the hydrocarbon recovery is maximum. He also suggested standard measurements for gas relative permeability would not be applicable and special three phase relative permeability measurements are required to explain the phenomenon of gas displacement by water and the flow resulting from gas expansion.

Experimental work performed at The University of Texas at Austin by Du et al.[21], Walker et al.[22] and Al-Anazi et al.[23] focused on using methanol for treating condensate and water blocking. Their experiments showed considerable improvement in oil and gas relative permeability after methanol treatment especially in the case of high water saturation. They also reported an optimum volume of methanol injection after which the improvement is negligible.

Hydraulic fracturing has also been suggested as a useful technique to enhance gas productivity. A hydraulic fracture increases the available fluid flow area, thus reducing draw down and increasing the bottom hole flow pressure. Thus condensate formation does occur but is delayed as wells can be produced at higher bottom hole pressures.

Settari et al.[34] conducted simulations and reported that hydraulic fracturing can restore up to 50-70% of the PI loss due to condensate blocking. His simulations were based on hydraulic fracturing in the Smorbukk field. He observed that PI improvement is more sensitive to the fracture length in low permeability zones and fracture conductivity is the more important parameter in high permeability zones.

Al-Hashim et al.[35] performed a simulation study which looked at the improvement in PI in hydraulically fractured wells. He reported that fracturing increases the time at which the dew point pressure is reached during depletion as compared to the non-fractured case.

Mohan et al.[36, 37] reported that the productivity improvement due to hydraulic fracturing of a gas condensate well is greatest for low permeability reservoirs. Parameters such as fracture dimensions and fracture conductivity are major contributors to improvement. He also suggested that these parameters also impact the productivity improvement, proppant volume, reservoir permeability, fracture permeability, fluid composition and condensate bank width.

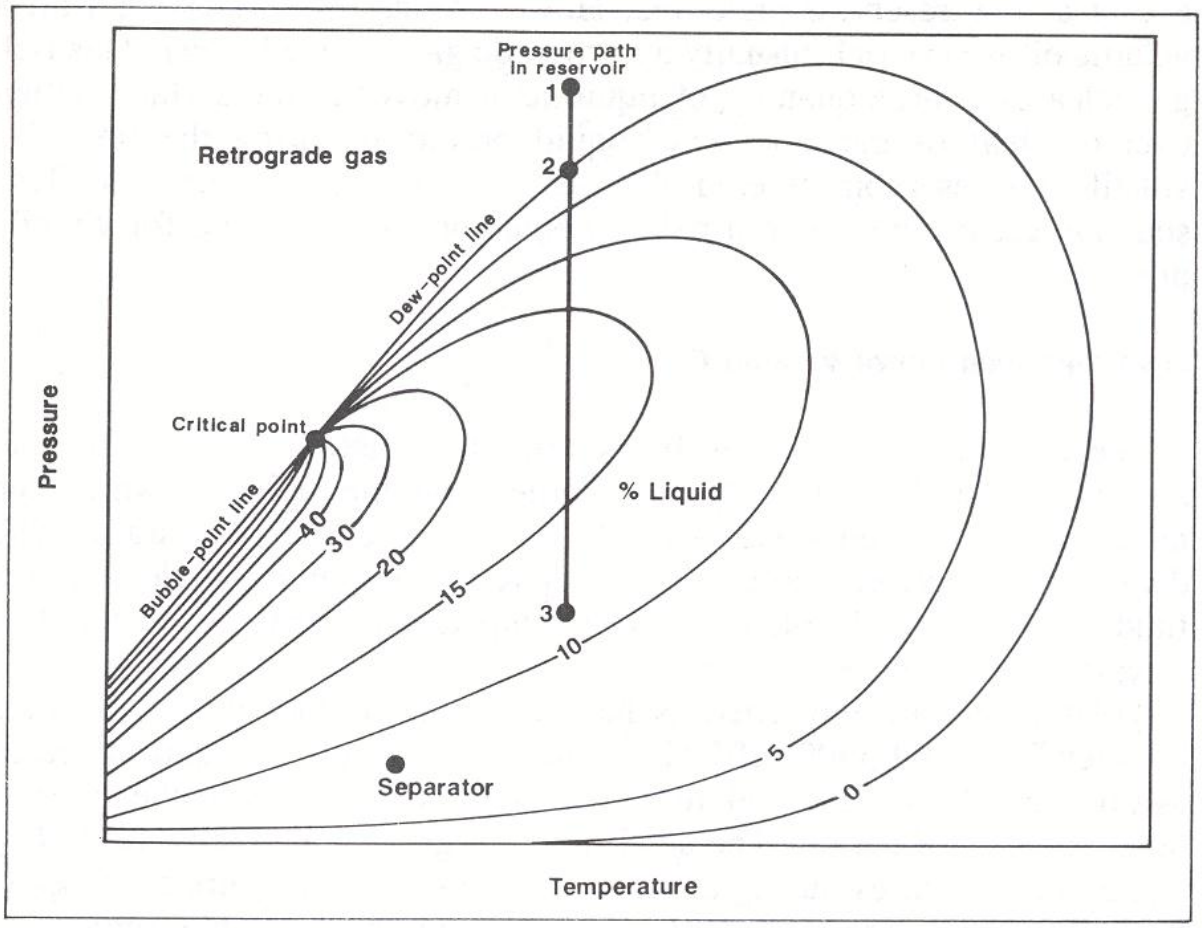

Figure 2.1 Phase diagram of a retrograde gas condensate reservoir [38]

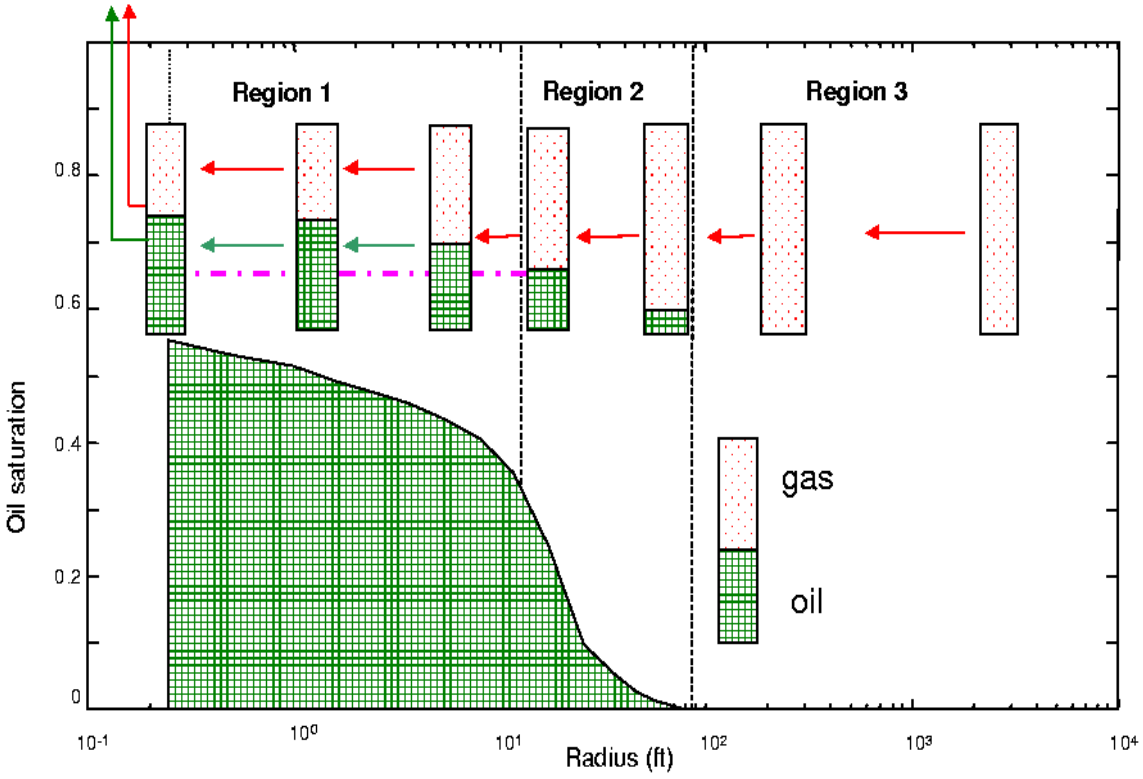

Figure 2.2 Schematic diagram of typical gas condensate flow regions [39]

CHAPTER 3: WETTABILITY

Wettability is a tendency for one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids. The fluid that spreads or adheres to the surface is known as the wetting fluid. In a petroleum reservoir, the solid surface is the reservoir rock which may be sandstone, limestone, or dolomite, together with cementing material and the fluids are water, oil and gas. Normally, either water or oil is the wetting phase while gas is always a non-wetting phase[40].

When the rock is water-wet, there is a tendency for water to occupy the small pores and to contact the majority of the rock surface. Similarly, when the rock is oil wet, the rock is preferentially in contact with the oil; the location of the two fluids is reversed from the water-wet case, and oil will occupy the small pores and contact the majority of the rock surface. It is important to note, however, that the term wettability is used for the wetting preference of the rock and does not necessarily refer to the fluid that is in contact with the rock at any given time.

For example, consider a clean sandstone core that is saturated with refined oil. Even though the rock surface is coated with oil, the sandstone core is still preferentially water-wet. The wetting preference can be demonstrated by allowing water to imbibe into the core. The water will displace the oil from the rock surface indicating that the rock surface prefers to be in contact with water rather than oil. Similarly, a core saturated with water is oil-wet if oil will imbibe into the core and displace water from the rock surface. This effect is quantified in the combined USBM-Amott method for measuring wettability[41].

Depending on the specific interactions of rock, oil, and brine, the wettability of a system can range from strongly water-wet to strongly oil-wet. When the rock has no strong preference for either or water, the system is said to be of neutral or intermediate wettability. Besides strong and neutral wettability, a third type is fractional wettability, where different areas of the core have different wetting preferences.

The wettability of the rock fluid system is important because it is a major factor controlling the location, flow and distribution of fluids in a reservoir. When the system is in equilibrium, the wetting fluid will completely occupy the smallest pores and be in contact with a majority of the rock surface (assuming, of course, that the saturation of the wetting fluid is sufficiently high). The nonwetting fluid will occupy the centers of the larger pores and form globules that extend over several pores.

FRACTIONAL WETTABILITY

The realization that rock wettability can be altered by absorbable crude oil components led to the idea that heterogeneous forms of wettability exist in reservoir rocks. Generally, the internal surface of reservoir rock is composed of many minerals with different surface chemistry and adsorption properties, which may lead to variations in wettability. Fractional wettability also called heterogeneous, spotted, or Dalmation wettability was proposed by Brown and Fatt[42]. In fractional wettability, crude oil components are strongly adsorbed in certain areas of the rock, so a portion of the rock is strongly oil-wet, while the rest is strongly water-wet. Note that this is conceptually different from intermediate wettability, which assumes that all portion of the rock surface have a slight but equal preference to being wetted by water or oil.

MIXED WETTABILITY

It is generally accepted that all rocks were initially water wet. Salathiel[43] introduced the term mixed wettability for a special type of fractional wettability in which the oil-wet surfaces form continuous paths through the larger pores. The smaller pores remain water-wet and contain no oil. The fact that all of the oil in a mixed wettability core is located in the lager oil-wet pores causes a small but finite oil permeability to exist down to very low oil saturations. This in turn permits the drainage of oil during a waterflood to continue until very low oil saturations are reached. Note that the main distinction between mixed and fractional wettability is that the latter implies neither specific locations for the oil-wet surfaces nor continuous oil-wet paths.

Basu et al.[44] investigated the theory behind rocks getting mixed wet. They proposed two possible explanations. They said that mixed wettability occurs due to surfactants dissolving and diffusing through the aqueous medium separating them from the rock surface and getting adsorbed on the rock surface. The other explanation was the collapsing of aqueous films under capillary pressure, allowing the oil to directly contact the mineral surface.

3.1 METHODS TO MEASURE WETTABILITY

Different methods have been used for the categorization of wettability. Two groups of methods are generally used

1. Quantitative methods:

- Contact Angle Method
- Amott
- Amott-Harvey
- Combined Amott-USBM method

2. *Qualitative methods*:

- Imbibition rate
- Microscopic examination
- Capillary pressure curves
- Relative permeability/saturation relationship

Unfortunately none of the methods is generally accepted which leads to ambiguities when comparing data from different sources and from different dates. Many wettability measurements are also imprecise, particularly near neutral wettability; therefore one should be cautious using literature data and conclusions. Although the Amott method is the most accurate, it is the most time-consuming method as well. Because they are quick and easy to perform drop imbibitions and contact angle tests were conducted to assess the changes in wettability in this study.

3.2 INTRODUCTION AND USE OF SURFACTANTS FOR WETTABILITY ALTERATION

The use of surfactants in the oil industry is not a new trend. Over the years, surfactants have been used for increasing oil recoveries, increasing mobility ratios and for different drilling processes.

There are mainly two mechanisms behind the use of surfactants i.e. reduction in oil-water interfacial tension and alteration of rock wettability. Austad et al.[45] and Spinler et al.[46] have shown with experimental results that surfactants can alter the wettability from an oil-wet to a water-wet state. Standnes[47] conducted imbibition and contact angle tests which showed the wettability being altered from oil-wet to water-wet. Most traditional surfactant floods were conducted to minimize the interfacial tension between

oil and water. In water-wet reservoirs, oil is generally trapped in pore spaces by capillary forces and can be present as discontinuous oil ganglia following a water flood. In such cases, by reducing the interfacial tension, the capillary forces are reduced leading to increased recovery. Although a reduction in IFT will help mobilize the oil, a change in wettability of the pore surfaces to more water-wet state will release oil from the surface leading to maximum improved recovery.

Wettability alteration can also be beneficial in fractured reservoirs where effective mass transfer of fluids is desired between matrix and the fracture. Surfactants are effective when the fractured formations are water wet, where capillary imbibition of surfactants from the fracture into the matrix contributes to oil recovery. Further, surfactants capable of altering wettability can be especially beneficial in oil wet fractured formations[48]. The surfactants in the fracture can enter the matrix, change the wettability and thus allow more imbibition pushing the oil out.

Surfactants have also been used in wells where liquid loading is a major problem. Liquid loading results in the buildup of water at the bottom of the bore hole exerting hydrostatic backpressure on the formation reducing gas production. Typical chemical solutions include batch or continuous injection of deliquification surfactants designed to reduce the surface tension of the liquid. This, in turn, allows gas entrainment and an effective reduction in liquid density. The critical velocity required to lift the liquids is reduced, allowing the well to return to continuous flow.

Drilling muds and completion fluids often contain surfactants to either suspend the components in the additive package or improve the drilling process[46]. For example, cationic and anionic surfactants are included in oil base muds to wet the surface of the cuttings and facilitate their removal from the wellbore by flotation. It has been suggested that drilling fluids containing surfactants can change the wettability of the core and that

oil based muds have the most profound change on the wettability of both sandstone and carbonate outcrop rocks. Sanner[49] and McDonald[50] also confirmed that oil based mud filtrate is the main cause behind wettability reversal of the rocks.

3.3 SURFACTANT CHEMISTRY

Surfactants are compounds that lower the surface tension of a liquid, allowing easier spreading, and lowering of the interfacial tension between two liquids, or between a liquid and a solid They have a characteristic structure, which involves at least one hydrophobic (water-hating) and one hydrophilic (water-loving) functional group. The molecular structure of surfactants is such that the hydrophobic part likes to be as far away from the aqueous phase as possible while the hydrophilic part likes to remain in contact with the water.

In case of an aqueous media, surfactant molecules will move to the air/water and solid/water interfaces and orient themselves so the contact between the hydrophobic groups and the water can be minimized. The hydrophobic tail of the molecule aligns itself to the less polar liquid while the hydrophilic head orientates itself towards the more polar liquid. The molecular interaction at the interface occurs between the hydrophilic head of the surfactant and the polar phase molecules and between the hydrophobic tail of surfactant and the non-polar phase molecules. This results in reduction of interfacial tension as the newly developed interactions are stronger than the interaction between the non-polar and polar molecules. Surfactant at low concentration has a tendency to adsorb at the surface or interface and significantly reduce the amount of work required to expand those interfaces. The stronger the tendency, the better the surfactant and the denser the surfactant packing at the interface, the larger will be the reduction in surface tension[51].

Surfactants fall in the following classifications according to the nature of the hydrophilic group

- Anionic: hydrophilic head is negatively charged;
- Cationic: hydrophilic head is positively charged;
- Nonionic: hydrophilic head is polar but not fully charged
- Amphoteric: molecule has both potential positive and negative groups; charge depends on pH of the medium.

3.4 FLUORINATED SURFACTANTS

In fluorinated surfactants, the hydrophobic part of the surfactant molecule contains fluorine. At least one hydrogen atom in the hydrophobic segment of the surfactant has been replaced by fluorine. Both the extent of fluorination and the position of fluorine atoms in the surfactant molecule affect the characteristics of the surfactant. Hence, fluorinated surfactants can be classified as per fluorinated surfactants or partially fluorinated surfactants. In per fluorinated surfactants, all hydrogen in the hydrophobic segment has been replaced by fluorine. In partially fluorinated surfactants, the hydrophobic part of the surfactant molecule contains both fluorine and hydrogen atoms[52].

Substitution of fluorine for hydrogen changes the properties of a surfactant drastically. The hydrophobic part of the fluorinated surfactant not only repels water but repels oil and fat as well. Hence, fluorinated surfactants exhibit both water and oil repellency when adsorbed on substrates such as textiles or paper. Fluorinated surfactants are more surface active than their hydrocarbon counterparts. Fluorinated surfactants can lower the surface tension of aqueous systems to below 20 mN/m and are effective at very low concentrations. Only 10 ppm of a fluorinated surfactant may be needed to lower the surface tension of water to 40 mN/m[52].

CHAPTER 4: ANALYTICAL METHODS

This chapter provides a brief explanation of the analytical methods used in this research to evaluate chemical treatments for wettability alteration.

4.1 SOLUBILITY/COMAPTIBILITY TESTS FOR SOLVENT SELECTION

Kumar et al.[22] showed that treatments using surfactants (FC-X in this case) delivered in a mixture of methanol and water improved gas and condensate relative permeabilities. However, they also showed that treatment of sandstone cores did not produce any improvement in presence of connate water. Thus, it was thought that this phenomenon might be due to incompatibility of the treatment solution and the brine. Therefore, the following characteristics are desired for the solvent which is being used to deliver the surfactant to the rock surface.

- Treatment solution (surfactant + solvent) should be soluble with reservoir brine at the expected S_{wi} and reservoir temperatures. Solubility of the surfactant in the solvents decreases with increasing water concentration and temperature and eventually reaches a cloud point. This is typical of non-ionic surfactants.
- The treatment solution should be able to dissolve the salts present in the connate brine and should not damage the reservoir permeability.
- The solvent mixture should have a low viscosity and reasonable volatility to be produced back after the well is returned to production.
- It should satisfy the environmental regulations
- It must be cost effective.

Many gas/gas-condensate reservoirs are associated with high water saturation and very high salinity brines. Precipitation of either the surfactant as it reaches a cloud point and/or salt (if the solvent is not able to solubilize high salt concentrations) can result in undesirable effects such as a reduction in rock permeability. The cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble and precipitate or the liquids are no longer miscible and form a second phase giving the fluid a cloudy appearance. Reservoir conditions; brine salinity, water saturation, and temperature vary and therefore different solvent mixtures may be required for delivering the surfactant depending on the specific conditions. Solvents are selected based on either recommendation from the chemical manufacturer or from past experience working with any specific class of materials.

The solubility, stability, and compatibility between the chemical and the solvent and between the treatment (chemical + solvent) and the reservoir brine were assessed by a series of phase behavior tests. The first step was to prepare the treatment with its associated solvent at varying concentrations and look for phase separation, if any. This helps to decide if there is compatibility between the chemical and the solvent and also to determine each chemical's solubility limit. After this test, the selected treatment solution was mixed with reservoir brine at varying ratios at room and experimental temperatures. The samples were observed over time to see if they were stable i.e. no phase separation or precipitation occurred. The observation of more then one phase, a cloudy or opaque phase, or any solid phase was considered as an indication of an un-stable solution.

4.2 COREFLOOD EXPERIMENTS

This following discussion describes the experimental setup that was used to perform core flood experiments. It contains a description of the equations used and the apparatus used for performing the core floods. Finally, the methodology for conducting these core floods is explained.

Principle

The experimental core floods are based on Darcy's law

$$k = \frac{q \mu L}{A \Delta P}$$

Where

q = flow rate in the core

μ= Fluid viscosity

L= length of the core

A= cross-sectional area of the core

ΔP= pressure drop (steady state) across the length of the core.

Forchheimer suggested that Darcy's law becomes invalid at high velocities and the flow contribution due to non-Darcy flow needs to be included to calculate the correct single-phase gas permeability. For non-Darcy flow, the single-phase permeability was calculated using the equation proposed by Forchheimer:

$$\frac{\Delta P}{L} = \frac{u \mu}{k} + \beta \rho u^2$$

Where

u= Darcy velocity

ρ= Fluid density

β = non-Darcy flow coefficient.

When re-arranged, this equation gives us a slope equation in which μ/k is the intercept and βρ as the slope. The intercept and slope were used to calculate k and β

$$\frac{\Delta P}{uL} = \frac{\mu}{k} + \beta \rho u$$

We know that the relative permeability (k_{ri}) of each phase i is defined as

$$k_{ri} = \frac{k_i}{k}$$

Where k_i is the permeability of fluid i and k is the initial gas permeability at 100% gas saturation at low velocity. Now, the two-phase relative permeability of each phase i at steady-state can be calculated using Darcy's law:

$$k_{ri} = \frac{q_i \, \mu_i \, L}{k \, A \, \Delta P_i}$$

Where i refer to either gas or oil (condensate) phase. For gas condensate fluids, the interfacial tension between the phases is small and thus the capillary pressure is negligible compared to the measured pressure drop across the core. Thus, the pressure drop of each phase is equal ($\Delta P_g = \Delta P_o = \Delta P$).

Mass balance in the core

Oil and gas flow rates in the core derived from the mass balance are

$$q_o = \frac{f_o \, q \, \rho}{f_o \, \rho_o + f_g \, \rho_g}$$

$$q_g = \frac{f_g \, q \, \rho}{f_o \, \rho_o + f_g \, \rho_g}$$

Where

q = total flow rate of single phase gas mixture above the dew-point pressure

ρ = molar density of single phase gas mixture above the dew-point pressure

q_g = flow rate of gas-phase at a pressure below the dew-point pressure

q_o = flow rate of oil-phase at a pressure below the dew-point pressure

f_g = fractional flow of gas-phase at a pressure below the dew-point pressure

f_o = fractional flow of oil-phase at a pressure below the dew-point pressure

ρ_g = molar density of gas-phase at a pressure below the dew-point pressure

ρ_o = molar density of oil-phase at a pressure below the dew-point pressure

At steady state the fractional flow of gas and oil (condensate) are equal to the volumes of gas and liquid obtained from constant composition expansion measurements at core pressure and temperature, expressed as a fraction of the total hydrocarbon volume. The density of each phase and the liquid dropout were calculated using the Peng-Robinson Equation of State (PREOS) at the experimental conditions. The flow rate of each phase through the core was calculated using above equations.

The coreflood apparatus was designed for high-pressure (5,000 psi) and high-temperature (300 ^{o}F) experiments. Figure 4.1, 4.2 & 4.3 show the core flood setup. High-pressure Quizix pumps were used to inject fluid at a constant rate. In some experiments multiple pressure ports were used to measure pressure drop across four sections (2 inches in length each) of the core. Two backpressure regulators were used to control the flowing pressure upstream (BPR-1) and downstream (BPR-2) of the core. BPR-1 maintains the fluid mixture above the dewpoint pressure and BPR-2 controls the core pressure and is maintained at a pressure below the dew point pressure. The core is kept vertical to prevent gravity segregation during two and three phase flow. The core

holder, backpressure regulators, fluid accumulators, and flow lines are inside a temperature-controlled, forced-air circulation oven at a fixed temperature.

Outcrop cores of 1 inch diameter and 8 inches in length were cut from a block of Berea Sandstone or Texas Cream Limestone. The cores were dried in an oven at 180°C for 12 hrs and then weighed. The selected core was the wrapped with Teflon tape Aluminum foil was then wrapped over the Teflon tape followed by a piece of Teflon heat-shrink using a heat gun; this was done to prevent injected fluids from contacting the Viton rubber sleeve. The wrapped core was placed into a core holder and put inside an oven overburden pressure was then applied using a hydraulic hand pump with pump oil as the confining fluid. The initial water saturation was established by injecting a known volume of brine into vacuumed core at room temperature while for some experiments the Swi was established at experimental temperature using a flow loop. Gas condensate mixtures were prepared using normal hydrocarbons such as; methane, propane, n-butane, n-heptane, n-decane, n-dodecane and n-pentadecane. Two combinations of sample mixtures are shown in table 4.1 and table 4.2.

The initial dry gas permeability of the core was measured using either nitrogen or methane at room temperature. BPR-1and BPR-2 were typically set around 3,000 psig and 1,000 psig respectively. Initial water saturation was then established. The core was then shut-in for at least one hour and followed with a nitrogen or methane flood to distribute water uniformly throughout the core and to measure the gas permeability at initial water saturation. Two-phase flow with the gas condensate mixture was conducted using the dynamic flashing method. The upstream back-pressure regular is set above the dew point pressure and is then flashed in the core below the dew point pressure established by the downstream back-pressure regulator. The gas mixture was injected at a known constant flow rate which allows the condensate to dynamically accumulate in the core in a way

that is similar to condensate accumulation in the near wellbore region at pressures below the dew point. Steady-state pressure drop across the core was measured at multiple rates and relative permeabilities for gas and oil were calculated.

Treatment solution was then injected and the core was shut-in for a minimum of 15 hours to let the treatment adsorb to the rock. This was followed with a post-treatment gas-condensate flood using the same gas mixture and conditions as the initial pre-treatment gas condensate flood; the improvement factor was then calculated for the pre and post-treatment flood. Finally, the single phase permeability is measured again with dry gas to check if damage such as plugging or rock degradation has occurred to the core during the chemical treatment.

4.3 X-RAY PHOTO ELECTRON SPECTROSCOPY (XPS)

Swedish physicist Kai Siegbhan and his group in Uppsala (Sweden) in mid 1950's developed a high-resolution beta-ray spectrometer capable of resolving Robinson's smears into distinct peaks. In 1954, they recorded the first high energy resolution XPS spectrum of cleaved sodium chloride (NaCl) revealing the potential of XPS. They found each peak was characteristic of a particular electron shell from a particular atom but also that chemical bonding effects were reflected in the detectable peak shifts. The development of quantum mechanics in the late 1920s allowed the peak intensities to be interpreted as a quantitative measure of the composition of the sample surface. Siegbahn unveiled electron spectroscopy for chemical analysis in 1967. In cooperation with Siegbahn, Hewlett-Packard in the USA produced the first commercial monochromatic XPS instrument in 1969. Siegbahn was awarded the Nobel Prize in 1981 for his contribution to the development of high resolution electron spectroscopy[53].

Working Principle

XPS also known as ESCA (Electron Spectroscopy for chemical analysis) is based on the photoelectric effect. It is a surface analysis technique with a broad range of applications effective for qualitative elemental analysis (for all elements except hydrogen, H, and helium, He) and a quantitative analysis to estimate the chemical state and composition of a surface by the irradiation of soft X-rays into the sample.

The photoelectric effect refers to the emission, or ejection, of electrons from the surface of, generally, a metal in response to incident light. Energy contained within the incident light is absorbed by electrons within the metal giving the electrons sufficient energy to be emitted from the surface of the metal. In XPS tests, the method consists of irradiating a sample with monochromatic x-rays, resulting in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume. XPS results are initiated from the top of the sample between 5-12 nm of the surface layers since the applied soft X-ray excitation is not detrimental to the surface layers. Figure 4.4 describes the operating mechanism of XPS analysis.

Einstein assumed that a photon would penetrate the material and transfer its energy to an electron and this relation is given by:

$E = h\nu$

Where

h : plank constant (6.62×10-34 J.s)

ν: frequency of radiation (Hz)

The sample used for experimental study is placed under a beam of an X-ray source in an Ultra-High Vaccum (UHV) chamber. It is important to perform experiments under this condition because only the electrons emitted from the atoms close to the surface will have any chance of escaping the sample without colliding with another

particle. A hemispherical sector analyzer is used to detect electrons at different energy levels. Al-Kα (hν = 1486.8 eV) and Mg-Kα (hν = 1253.6 eV) X-rays sources are the two most common anodes used. The sample under study is subjected to irradiation by a high energy X-ray source. The ejected electron has a kinetic energy (KE) that is related to the energy of the incident beam (hν), the electron binding energy (BE), and the work function of the spectrometer (Φ). Thus, the binding energy of the electron can be calculated from

$$KE = h\nu - BE - \Phi$$

Where

KE: kinetic energy lank constant, eV

hν: energy of the photon

BE: binding energy

Φ: Work function of the spectrometer (calibrated before experiments)

A typical XPS spectrum is a plot of the number of electrons detected (Y-axis) versus the binding energy of the electron detected (X-axis). Each element produces a characteristic set of XPS peaks at characteristic binding energy values that directly identify each element that exist in or on the surface of the material being analyzed. These characteristic peaks corresponds to the electron configuration of the electrons with the atoms e.g., 1s, 2s, 2p, 3s etc. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element within the area (volume) irradiated[54].

Application of XPS analysis in the petroleum industry

Ramirez et al[55] used Auger Electron Spectroscopy (AES) and XPS to analyze the surface composition of Berea sandstone and the changes caused by contact with both salt and surfactant solutions comparing the surface results with the bulk composition. They concluded that the detection limits of the two techniques are different for different elements, so the results don't compare well because of the large uncertainties in the elemental sensitivity factors used in each method.

Mitchell et al.[56] used XPS and other spectrometric techniques for pore surface analysis of reservoir samples. They suggested that the direct analysis of the pore surface gives quick information pertaining to the wetting state which leads to better understanding of how reservoir quality and wetting state can be modified. They also proposed that XPS can be used to assess core wettability when compared to Amott wettability testing as this process takes more time.

Hill et al.[57] et al evaluated Imaging X-ray Photoelectron Spectroscopy (IXPS) in order to derive information on scale inhibitor distribution directly, and the wettability of pore surfaces indirectly from North Sea reservoir core samples. They also used XPS to analyze the effect of hot solvent cleaning indicating that core surface wettability characteristics are modified differently by different treatments. They concluded that surface analysis cannot be routinely applied to map inhibitor distribution or provide detailed correlation with core mineralogy.

Durand and Beccat[58] et al used XPS to investigate a possible direct relationship between surface carbon content and oil wettability. Reference clays were aged with crude oil or with crude oil plus brine. Clay size fractions from actual core samples were extracted, cleaned and submitted to the same procedure. After that, XPS was used for

surface analysis of the samples after each treatment. They concluded that avoiding carbon contamination is quite difficult, which makes it difficult to interpret the surface composition.

Toledo et al.[59] investigated the relationship between wettability and surface composition as determined from XPS for fracture surfaces of rocks. Their results provided quantifiable evidence that chemisorbed organic material on the pore surface can define the wetting character of rocks studied. Their results showed that oil-wetting and water-wetting indices of rocks correlate strongly with pore surface carbon content determined from XPS.

Testing Procedure

The following procedure was developed to prepare the XPS samples in a unique way to eliminate the effect of sample preparation as much as possible.

- Cut three-millimeter thick chips from one-inch diameter core samples.
- Age the samples by keeping them in the treatment solution (composed of chemical and solvent) at temperature over night.
- Take the samples out of the solution and blow air through the samples.
- Rinse the samples in the corresponding solvent and stir for 3 hours.
- Take the samples out of the solvent and blow air to remove the solvent.
- Dry the samples by keeping them at temperature overnight.

The chemicals were then rated based on the fluorine content on the sample's surface as reported from XPS. Those with high fluorine content, compared to others, were considered for further tests.

Table 4.1: A sample combination of gas condensate mixture to be used in core flood experiments

T = 275^{o}F	
Component	Mole %
Methane	93
n-Butane	4
n-Decane	2
n-Pentadecane	1

Table 4.2: A sample combination of gas condensate mixture to be used in core flood experiments

T = 175^{o}F	
Component	Mole %
Methane	86
Propane	6
n-Heptane	5
n-Decane	3

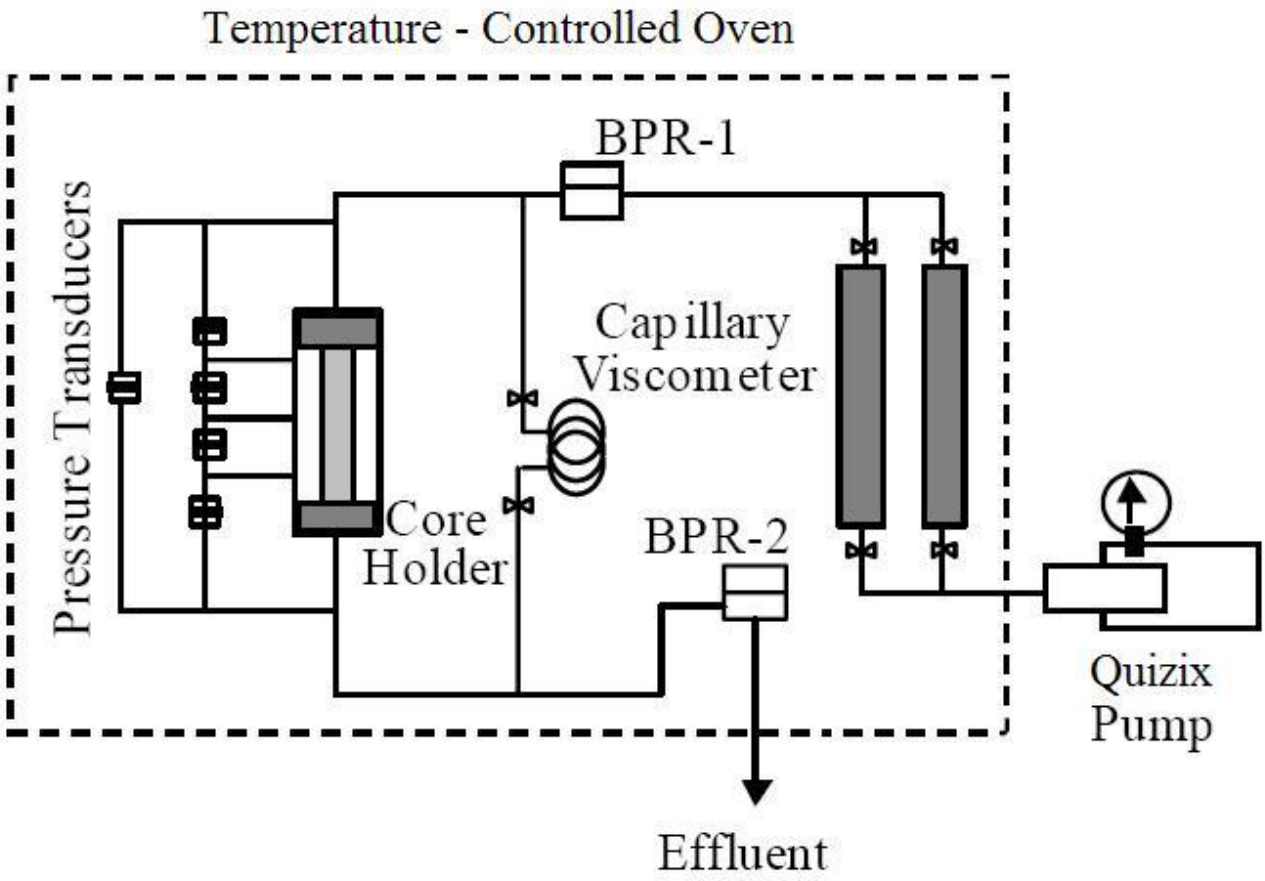

Figure 4-1: S Diagram of core flood experimental setup

Figure 4.2: Photograph of HTHP coreflood laboratory

Figure 4.3: Photograph of HTHP coreflood apparatus inside the oven

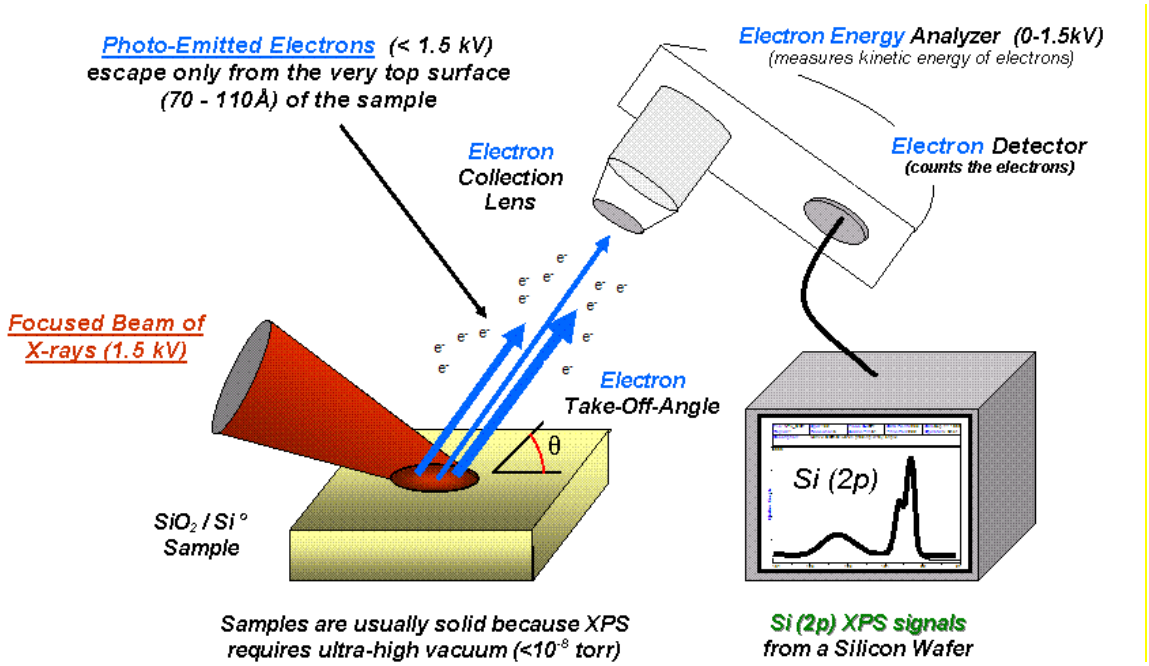

Figure 4.4: Schematic describing the operating principle of XPS[60]

CHAPTER 5: RESULTS AND DISCUSSION FOR BEREA SANDSTONE CORES

In this chapter results are presented for XPS analysis, wettability tests and core floods (conducted by other members of the research group). A comparison between these measurements shows that the results are correlated under certain conditions allowing us to use simple drop tests or XPS analysis as screening tests for fluoro-carbon surfactants.

METHODOLOGY

In terms of analyzing the chemical L-18961, the first step was to find a solvent that was able to solubilize this chemical at the experimental temperatures. After performing the stability/solubility test, the treatment solution was tested for compatibility with brine. The purpose of doing these compatibility tests is to simulate different brine concentrations as present in the reservoir and evaluate how these solvents react to varying brine concentrations at varying temperatures. Multiple treatment solutions with varying percentages of brine were prepared in different pipettes and observed for clear, cloudy and turbid conditions. Cloudy and turbid conditions were considered unstable while a clear solution means that the solvent is compatible with the chemical.

After the solvents for each chemical are selected based on the tests described earlier, drop tests were conducted on the treated rock chips to see if a wettability change is observed after treatment. Drop tests were performed with decane and water on treated and untreated chips.

As the drop tests show promise for changing the wettability of the rock, XPS tests were performed on treated chips to estimate the fluorine content on the chips. This

fluorine content would further suggest that the fluoro-surfactant has been deposited on the chip which in turn implies a change in wettability of the chip.

After performing XPS analysis on the chips, these chemicals are now ready to be tested in core flood experiments that mimic the actual reservoir conditions. Finally, the cores from the experiments were tested for fluorine presence across the core. Chips were taken from the top, middle and bottom of the core and fluorine content was estimated through XPS tests.

Every chemical was tested in the same sequence of tests. The results are outlined in the following discussion.

5.1 ANALYSIS FOR CHEMICAL L-18961

5.1.1 Stability/Compatibility Tests

For L-18961, butoxy ethanol-ethanol-IPA in the ratios of 60:30:10 and 50:30:20 were tried as solvents at different temperatures. The ratio of 60:30:10 was selected for the treatment as it is similar to other combinations that have been tried in the past. The results are shown in tables 5.1 and 5.2.

The results for stability test with the brine suggest that this specific treatment solution was stable only below brine concentration of 25%. The results of these tests are presented in tables 5.3 through table 5.6.

5.1.2 Drop Tests

Since the treatment solution was stable below 25% of brine concentration, drop tests were conducted on the treated rock chips to see if a wettability change is observed after treatment. Drop tests were performed with decane and water on treated and untreated chips. As expected, decane and water imbibed readily onto the untreated chips.

In the treated chips, however, decane imbibed into the sample in approximately ten seconds where as water didn't imbibe at all for more than one minute. This suggests that the treatment has altered the wettability of the initially water-wet rock to neutral wet. Figure 5.1 shows the picture of drop test taken 10 seconds after dropping water and decane on the treated chips. In the picture 'W' denotes water and 'D' denotes decane.

5.1.3 XPS on Chips

The results for the XPS tests do show significantly higher fluorine content for the treated chips as compared to the untreated chips as shown in figure 5.2.

5.1.4 Core Flood Results

After passing a series of screening tests that include solubility tests, compatibility tests, drop tests and XPS analysis on chips, the chemical L-18961 with butoxy ethanol / ethanol / IPA in the ratio of 60:30:10 was deemed acceptable for core flood experiments. The above treatment solution was used in four core flood experiments to observe its effectiveness. It proved to be a successful chemical for Berea as it yielded improvement factors above 1.5. Table 5.7 lists the important details and results of the core flood experiments.

5.1.5 XPS results from treated core

Table 5.8 lists the fluorine content across the 8" core for the core flood experiments. Experiment 176 was unique in that it was treated 3 times which explains the high fluorine content at the inlet of the core. There was a smooth decreasing trend of fluorine presence across the core as observed in Figure 5.3.

5.2 ANALYSIS FOR CHEMICAL L-20294

5.2.1 Stability/Compatibility Tests

Table 5.9 shows the results of the stability/solubility tests conducted for L-20294.After performing the stability/solubility test, the treatment solution was tested for compatibility with brine. The results for stability test with the brine that this specific treatment solution remained clear at all temperatures up to a brine concentration of 50% so it was concluded that this chemical is perfectly compatible with the solvent used. Table 5.10 shows the results of the conducted compatibility tests.

5.2.2 Drop Tests

After observing satisfactory performance with butoxy ethanol-ethnaol as a solvent, drop tests were conducted on the treated rock chips to observe any wettability change. As expected, decane and water imbibed readily onto the untreated chips. In the treated chips, decane imbibes more into the sample when compared to water didn't imbibe at all. This showed the treatment has altered the wettability of the initially water-wet rock to neutral wet as both drops (decane and water) sit up on the chip and doesn't imbibe. Figure 5.4 shows the picture of drop test taken approximately 40 seconds after dropping water and decane. In the picture 'W' denotes water and 'D' denotes decane.

5.2.3 XPS on Chips

The fluorine content from XPS tests do show significantly higher fluorine content for the treated chips as compared to the untreated chips as shown in figure 5.5.

5.2.4 Core Flood Results

After observing satisfactory performance in terms of solubility, stability and potential for wettability alteration, this treatment solution was used in two core flood experiments to observe its effectiveness. It proved to be a successful chemical for Berea as it yielded improvement factors above 1.99. Table 5.11 lists the important details and results of the core flood experiments.

5.2.5 XPS results from treated core

Table 5.12 lists the fluorine content across the 8" core for the core flood experiments. Core from the experiment 148 showed higher fluorine content than experiment 141 at the inlet of the core which is likely responsible for the higher improvement factor of 2.46. For both cores, a decreasing trend of fluorine concentration across the core was observed as shown in Figure 5.6.

5.3 ANALYSIS FOR CHEMICAL FC-X

5.3.1 Stability/Compatibility Tests

Propylene glycol-iso propyl alcohol (PG-IPA), IPA, ethyl alcohol (EtOH) and butoxy ethanol -ethanol (BE-EtOH) were tested as solvents for FC-X at different temperatures. Butoxy ethanol -ethanol (BE-EtOH) in the ratio of 70:30 was selected as the solvent as it remained clear at all temperatures.

In terms of compatibility, it was observed that this specific treatment solution remained clear at all temperatures up to a brine concentration of 46% so it was concluded that this chemical is perfectly compatible with the solvent used. Table 5.13 shows the results of the conducted compatibility tests.

5.3.2 Drop Tests

Drop tests were performed with decane and water being dropped on the treated chips and comparing their imbibition with untreated chips. As expected, decane and water imbibed readily onto the untreated chips. In the treated chips, decane imbibes more quickly into the sample when compared to water. This showed the treatment has changed the wettability of the initially water-wet rock to neutral wet as the both drops (decane and water) sit up on the chip and doesn't imbibe. Figure 5.7 shows the picture of drop test taken approximately 20 seconds after dropping water and decane. In the picture 'W' denotes water and 'D' denotes decane. Figure 5.8 shows the beneficial effect of 0.2 % dopamine mixed with the treatment as both water and decane molecule does not imbibe.

5.3.3 XPS on Chips

The results for the XPS tests do show higher fluorine content for the treated chips as compared to the untreated chips as shown in figure 5.9. The figure also contains the result of using dopamine with the treatment solution and the very high fluorine content associated with it. This result clearly shows that the dopamine helps in getting more fluorine on the surface. However, the use of dopamine is not considered favorable in the reservoir as it might start polymerizing and plugging the pore space.

5.3.4 Core Flood Results

The results for the two core flood experiments prove that FC-X works for Berea as improvement factors of above 1.9 were obtained. Table 5.14 lists the important details and results of the core flood experiments.

5.3.5 XPS results from treated core

Table 5.15 lists the fluorine content at three points; inlet, middle and outlet of the two cores. The core from experiment 163 showed higher fluorine content than

experiment 106 at the inlet of the core which is likely responsible for the higher improvement factor of 2.05. However, when compared to the other chemicals, FC-X shows lesser fluorine content on the rock with a quite similar improvement factor. For both cores, a decreasing trend of fluorine concentration across the core was observed as shown in Figure 5.10.

A plot containing all the XPS results conducted on sandstone cores is given in Fig 5.11. Fig 5.12 & 5.13 show the trend of improvement factor versus inlet & outlet fluorine content for Sandstones.

Table 5.1: Stability of chemical L-18961 in a three-alcohol solvent system

Chemical Conc., %	Solvent	Room Temperature	175 °F	250 °F
1	2BE-EtOH-IPA (60-30-10)	Clear	Clear	Clear
2	2BE-EtOH-IPA (60-30-10)	Clear	Clear	Clear

Table 5.2: Stability of chemical L-18961 in a three-alcohol solvent system

Chemical Conc., %	Solvent	Room Temperature	175 °F	250 °F
1	2BE-EtOH-IPA (50-30-20)	Clear	Clear	Clear
2	2BE-EtOH-IPA (50-30-20)	Clear	Clear	Clear

Table 5.3: Compatibility data for 2% L-18961 in 2BE-EtOH-IPA (60-30-10)

Brine Mass %	175 °F	230 °F	250 °F
25	Clear	Clear	Clear
30	Cloudy	Cloudy	Clear
35	Cloudy	Cloudy	Clear
40	Cloudy	Cloudy	Cloudy
45	Cloudy	Cloudy	Cloudy
50	Cloudy	Cloudy	Cloudy
55	Cloudy	Cloudy	Cloudy
60	Cloudy	Cloudy	Cloudy

Table 5.4: Compatibility data for 2% L-18961 in 2BE-EtOH-IPA (50-30-20)

Brine Mass %	Room Temperature	175 °F
5	Clear	Clear
10	Clear	Clear
15	Clear	Clear
20	Clear	Clear
25	Clear	Clear
30	Cloudy	Clear
35	Cloudy	Cloudy
40	Cloudy	Little Cloudy

Table 5.5: Compatibility data for 1% L-18961 in 2BE-EtOH-IPA (60-30-10)

Brine Mass %	Room Temperature	175 °F
5	Clear	Clear
10	Clear	Clear
15	Clear	Clear
20	Clear	Clear
25	Clear	Clear
30	Cloudy	Clear
35	Cloudy	Clear
40	Cloudy	Little Cloudy

Table 5.6: Compatibility data for 1% L-18961 in 2BE-EtOH-IPA (50-30-20)

Brine Mass %	Room Temperature	175 °F
5	Clear	Clear
10	Clear	Clear
15	Clear	Clear
20	Clear	Clear
25	Clear	Clear
30	Cloudy	Clear
35	Cloudy	Clear
40	Cloudy	Little Cloudy

Table 5.7: Core flood results with chemical L-18961 in 2BE-EtOH-IPA (60-30-10)

	Exp# 154	**Exp# 171**	**Exp# 176**	**Exp# 189**
K, md	129	274	149	211
Temperature, ^{o}F	155	250	155	250
Chemical	L-18961	L-18961	L-18961	L-18961
Solvent	BE / Ethanol / IPA (60/30/10)	BE/ Ethanol / IPA (60/30/10)	BE/ Ethanol / IPA (60/30/10)	BE / Ethanol / IPA (60/30/10)
Nc	1.03E-05	2.6E-05	1.76E-05	1.63E-05
Initial Krg	0.045	0.034	0.031	0.0423
Improvement Factor	1.93-1.78	1.51-1.42	3.22-1.36	2.57-0.94

Table 5.8: Amount of fluorine present with distance along the core for L-18961 (XPS test)

Distance along the core	**Fluorine Content**			
	Exp# 154	**Exp# 171**	**Exp# 176**	**Exp# 189**
0.5	3.09	2.61	33.12**	3.68
4	2.6	2.25	4.94	1.95
8	1.87	1.5	4.17	1.28
IF	1.93-1.78	1.51-1.42	3.22-1.36	2.57-0.94

** shows the fluorine content of the core that was treated thrice with the chemical

Table 5.9: Stability/Compatibility of chemical L-20294 in different solvents

Chemical Conc., %	Solvent	Room Temperature	175 °F	230 °F	280 °F
1	PG-IPA (70-30)	Undissolved	Clear	Clear	Clear
2	PG-IPA (70-30)	Undissolved	Clear	Clear	Clear
5	PG-IPA (70-30)	Undissolved	2-phase	2-phase	2-phase
1	IPA	Undissolved	Clear	Clear	Clear
2	IPA	Cloudy	Clear	Clear	NA
1	EtOH	Cloudy	Clear	Clear	NA
2	EtOH	Cloudy	Clear	Clear	NA
5	EtOH	Cloudy	Clear	Clear	NA
1	2BE-EtOH (70-30)	Clear	Clear	Clear	Clear
2	2BE-EtOH (70-30)	Clear	Clear	Clear	Clear
3	2BE-EtOH (70-30)	Clear	Clear	Clear	Clear
4	2BE-EtOH (70-30)	Clear	Clear	Clear	Clear
5	2BE-EtOH (70-30)	Clear	Clear	Clear	Clear

Table 5.10: Compatibility data for 2% L-20294 in 2BE-EtOH (70-30)

Brine Mass%	Room Temperature	175 °F
20	Clear	Clear
25	Clear	Clear
30	Clear	Clear
35	Clear	Clear
40	Clear	Clear
45	Clear	Clear
50	Clear	Clear

Table 5.11: Core flood results with chemical L-20294 in 2BE-EtOH (70-30)

	Experiment 141	**Experiment 148**
K, md	189	145
Temperature, ^{o}F	155	155
Chemical	L-20294	L-20294
Solvent	2BE-EtOH (70-30)	2BE-EtOH (70-30)
Nc	1.11E-05	1.73E-05
Initial Krg	0.038	0.030
Improvement Factor	1.99-1.62	2.46-1.32

Table 5.12: Amount of fluorine present with distance along the core for L-20294 (XPS test)

Distance along the core	**Fluorine Content**	
	Experiment 141	**Experiment 148**
0.5	12.97	20.56
4	11	7.06
8	4.63	4.22
IF	1.99-1.62	2.46-1.32

Table 5.13: Compatibility data for 2% FC-X in 2BE-EtOH (70-30)

Brine #	Brine Volume %	Room Temperature	175 °F	250 °F
1	18	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
1	22	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
1	27	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
1	32	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
1	36	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
1	41	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
1	46	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
1	0	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
1	100	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
2	18	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
2	22	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
2	27	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
2	32	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
2	36	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
2	41	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
2	46	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
2	0	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
2	100	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
3	18	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
3	22	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
3	27	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
3	32	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
3	36	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
3	41	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
3	46	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
3	100	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
4	18	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
4	22	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
4	27	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
4	32	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
4	36	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
4	41	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
4	46	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase
4	100	Clear - 1 Phase	Clear - 1 Phase	Clear - 1 Phase

Brine#1: 30 g/l NaCL

Brine#2: Crushed Silurian Dolomite 37.45 gm rock/250 cc NaCl Brine (30g/L)

Brine#3: Crushed Pink Dolomite 26 gm rock/250 cc NaCl Brine (30g/L)

Brine#4: Crushed Gelph Dolomite 38 gm rock/250 cc NaCl Brine (30g/L)

Table 5.14: Core flood results with chemical FC-X in different solvents

	Experiment 163	Experiment 106
K, md	191	181
Temperature, ^{o}F	180	275
Chemical	FC-X	FC-X
Solvent	2BE-EtOH (70-30)	IPA (29.5%), PG (69.5%)
Nc	1.40E-05	1.77E-05
Initial Krg	0.038	0.07
Improvement Factor	2.05-1.69	1.92-1.87

Table 5.15: Amount of fluorine present with distance along the core for FC-X (XPS test)

Distance along the core	**Fluorine Content**	
	Experiment 163	**Experiment 106**
0.5	4.78	3.92
4	4.6	1.77
8	2.47	1.51
IF	2.05-1.69	1.92-1.87

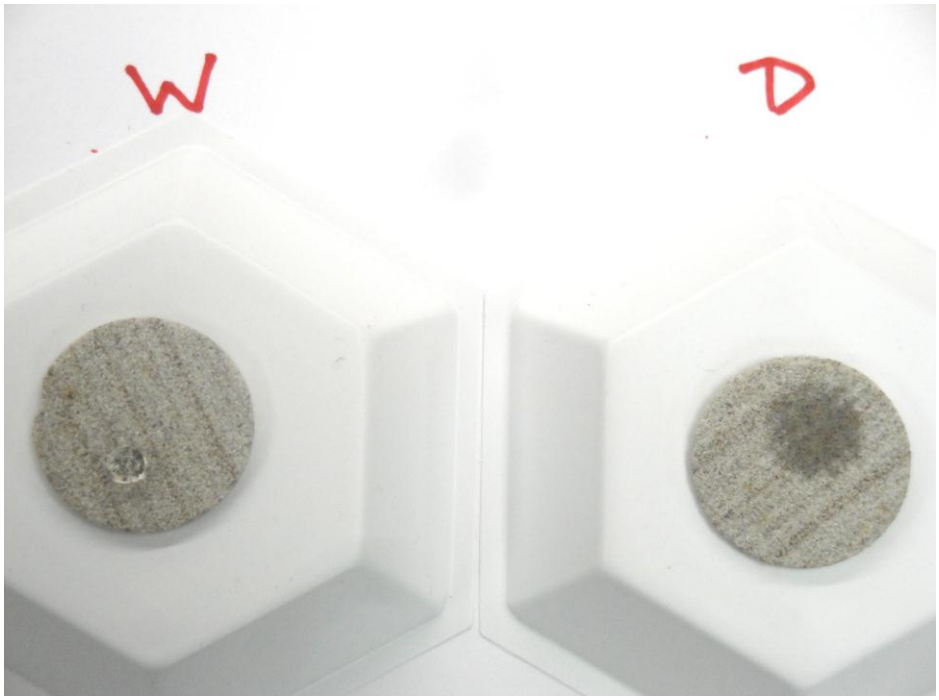

Figure 5.1: Drop tests on sandstone chips treated with L-18961. ‘W’ denotes water drop and ‘D’ denotes decane drop.

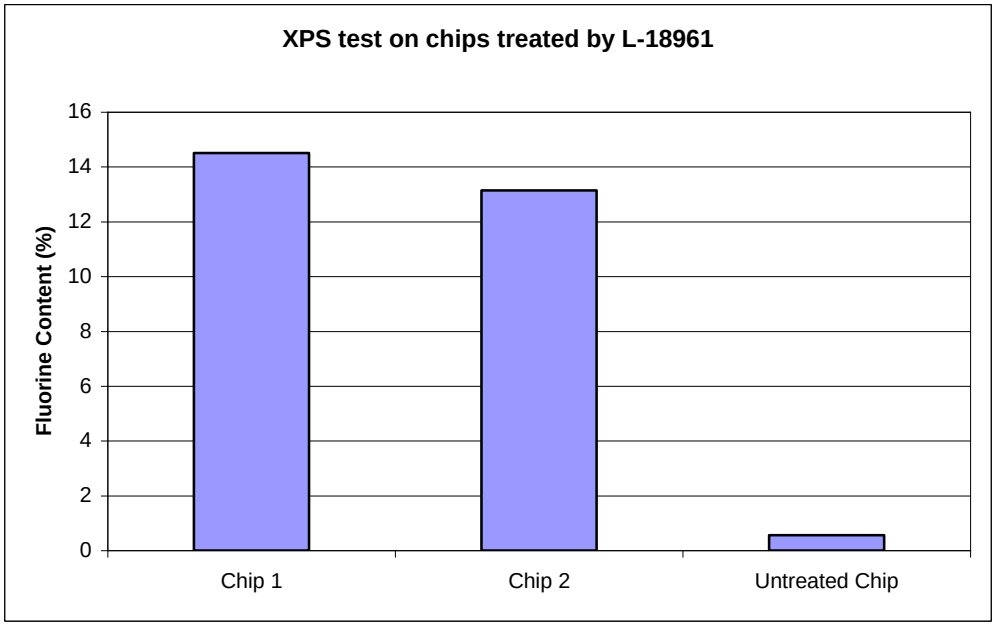

Figure 5.2: Fluorine content on sandstone chips treated with L-18961 (XPS tests)

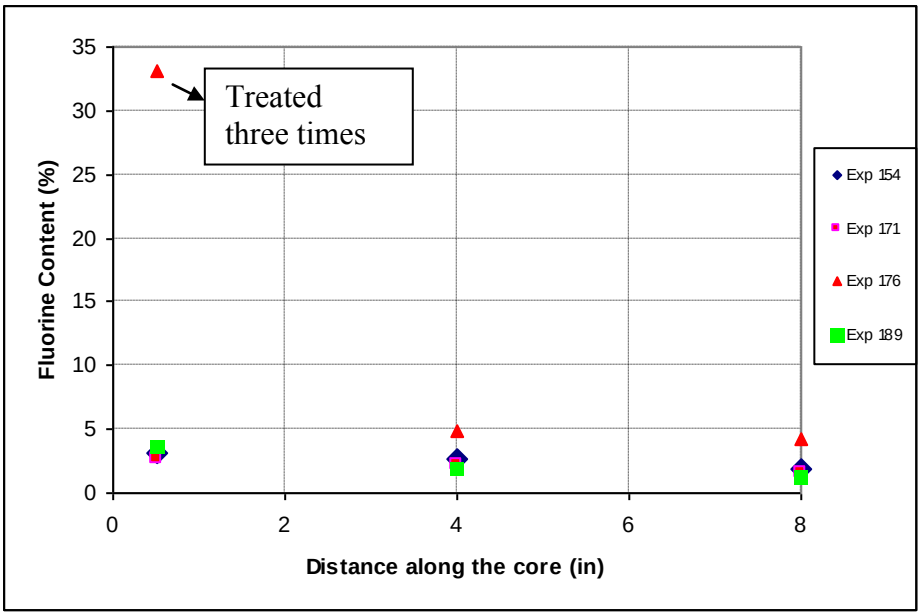

Figure 5.3: Plot of fluorine content versus distance along the core for different experiments for chemical L-18961

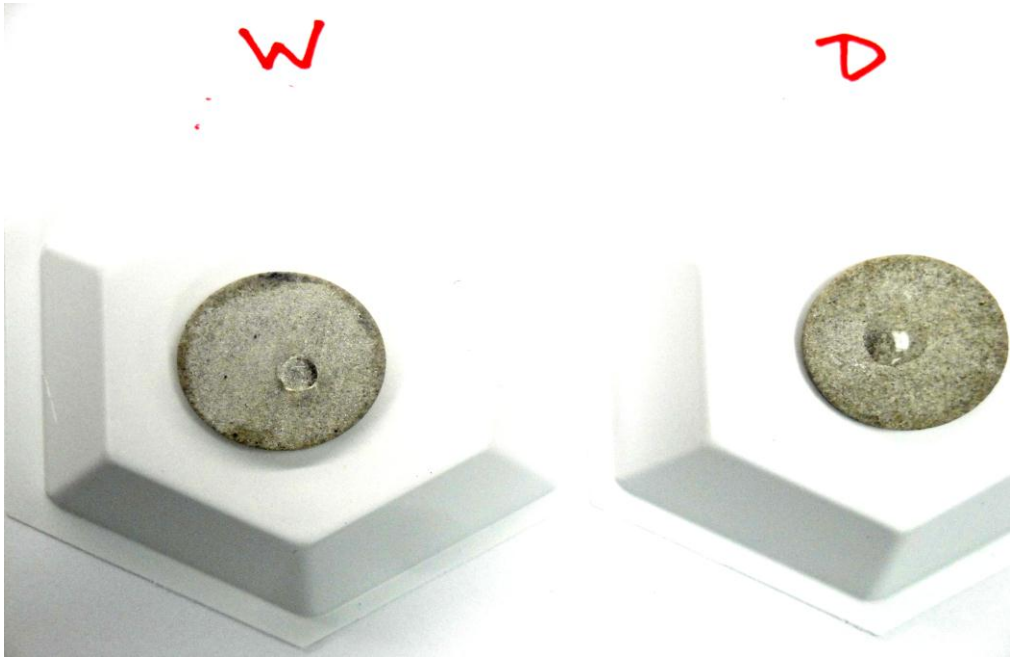

Figure 5.4: Drop tests on sandstone chips treated with L-20294. ‘W’ denotes water drop and ‘D’ denotes decane drop.

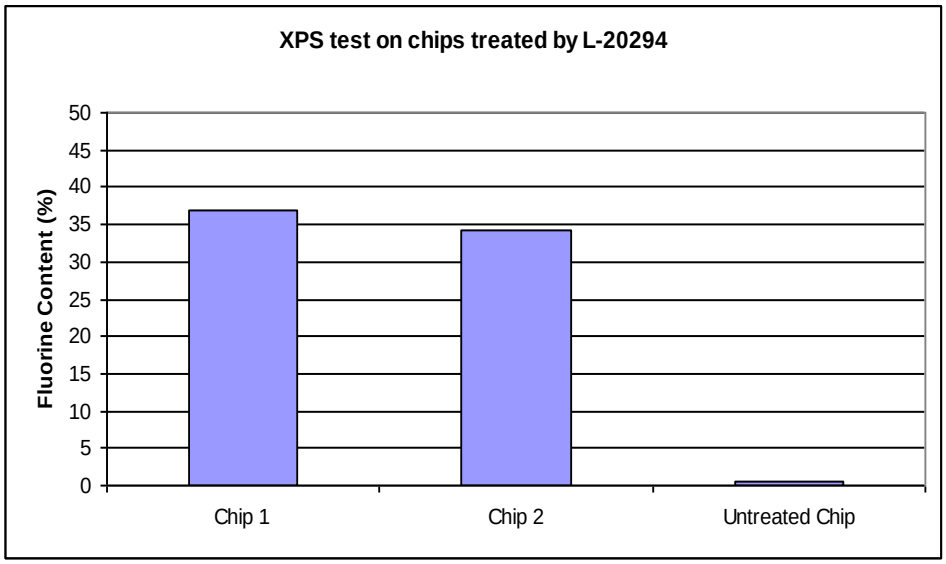

Figure 5.5: Fluorine content on sandstone chips treated with L-20294 (XPS tests)

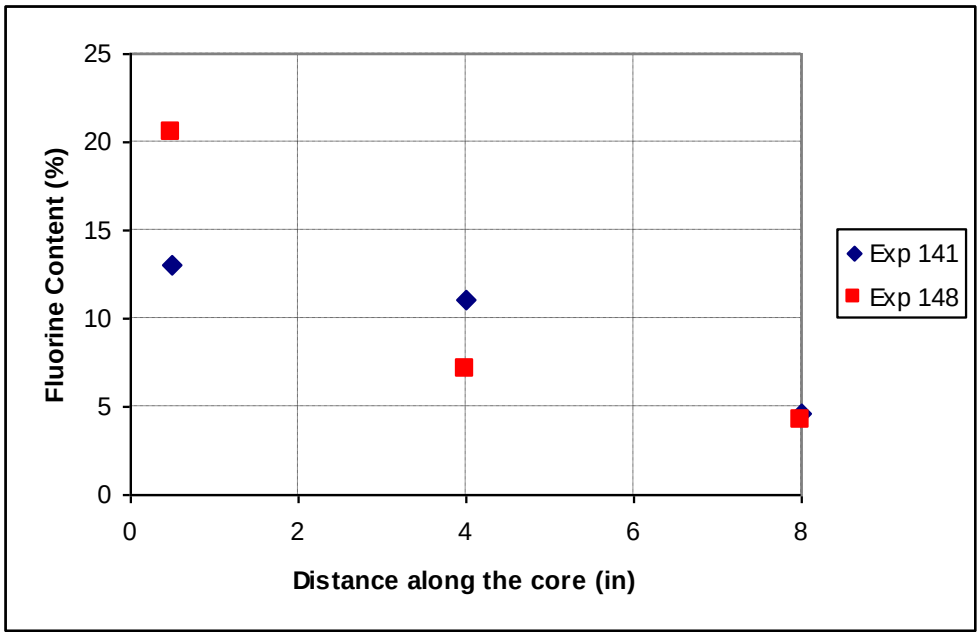

Figure 5.6: Plot of fluorine content versus distance along the core for different experiments for L-20294

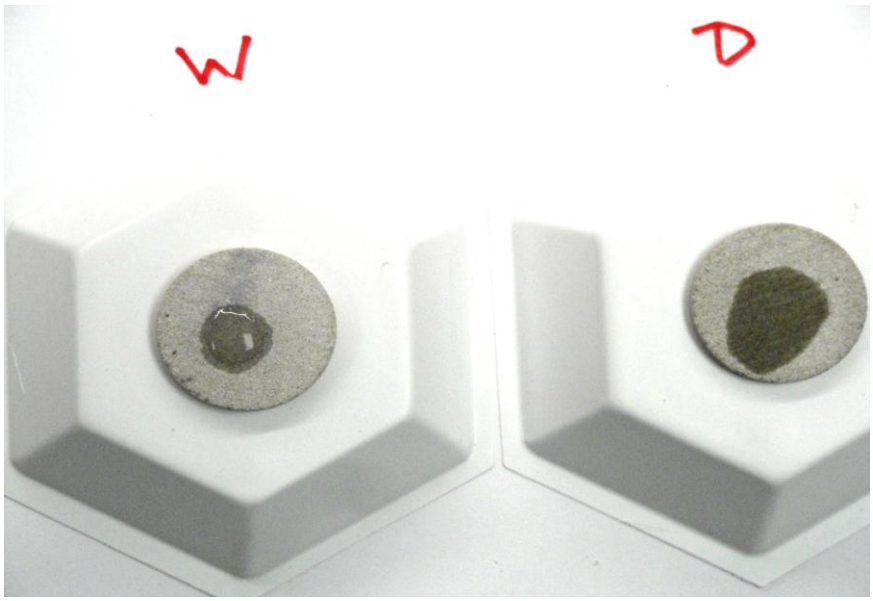

Figure 5.7: Drop tests on sandstone chips treated with FC-X. ‘W’ denotes water drop and ‘D’ denotes decane drop.

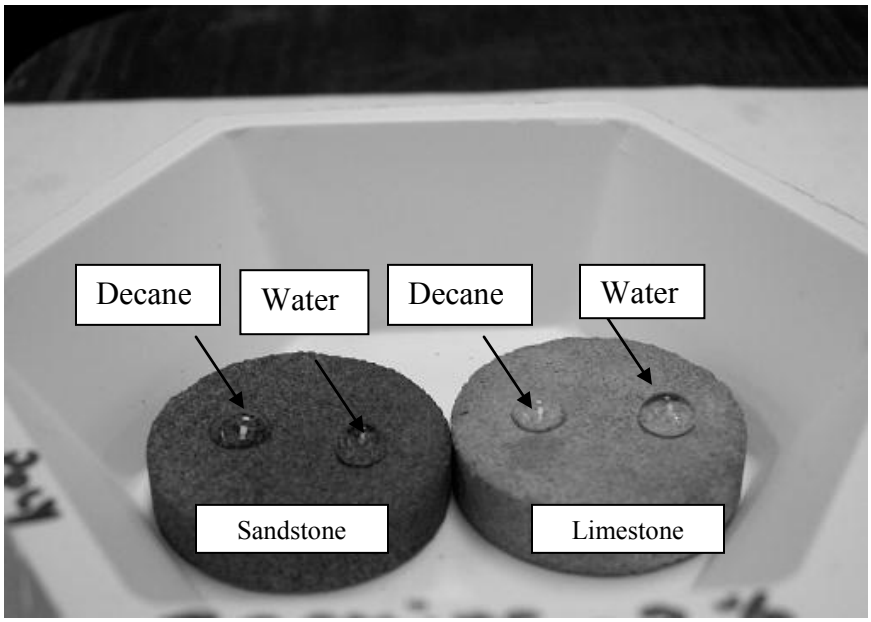

Figure 5.8: Drop tests on sandstone chips treated with FC-X mixed with Dopamine

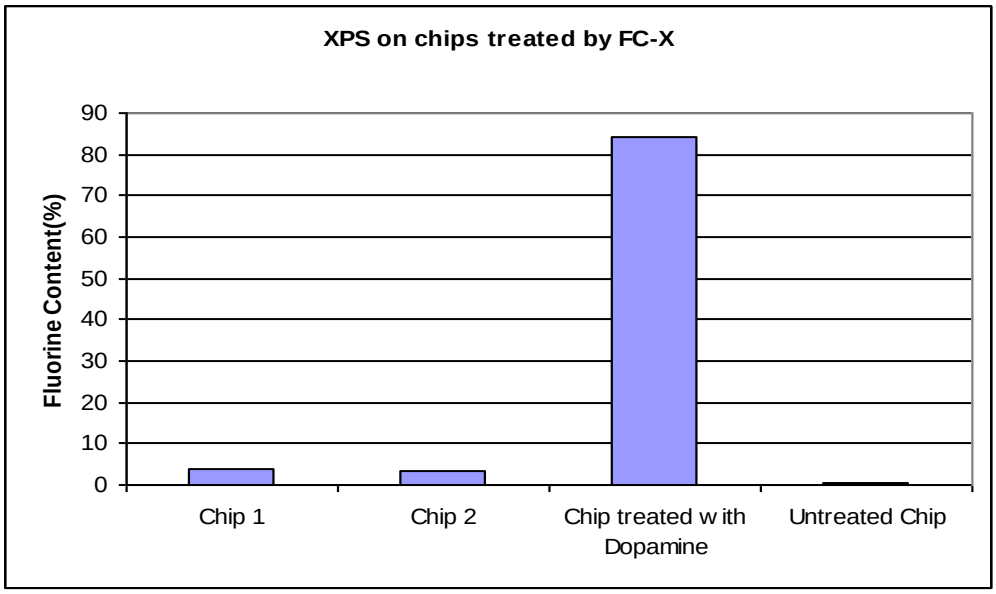

Figure 5.9: Fluorine content on sandstone chips treated with FC-X (XPS tests)

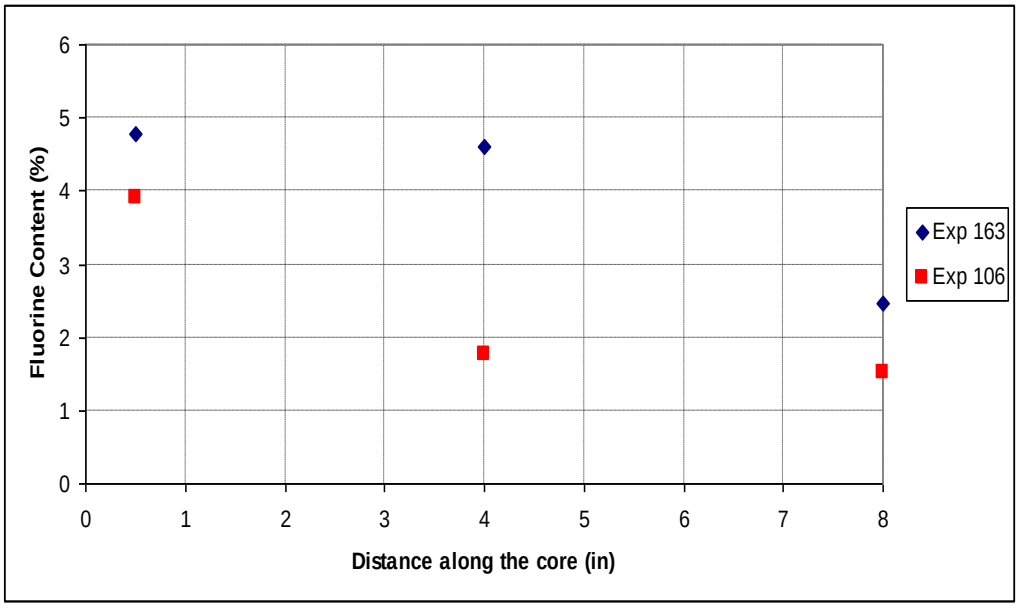

Figure 5.10: Plot of fluorine content versus distance along the core for different experiments for FC-X

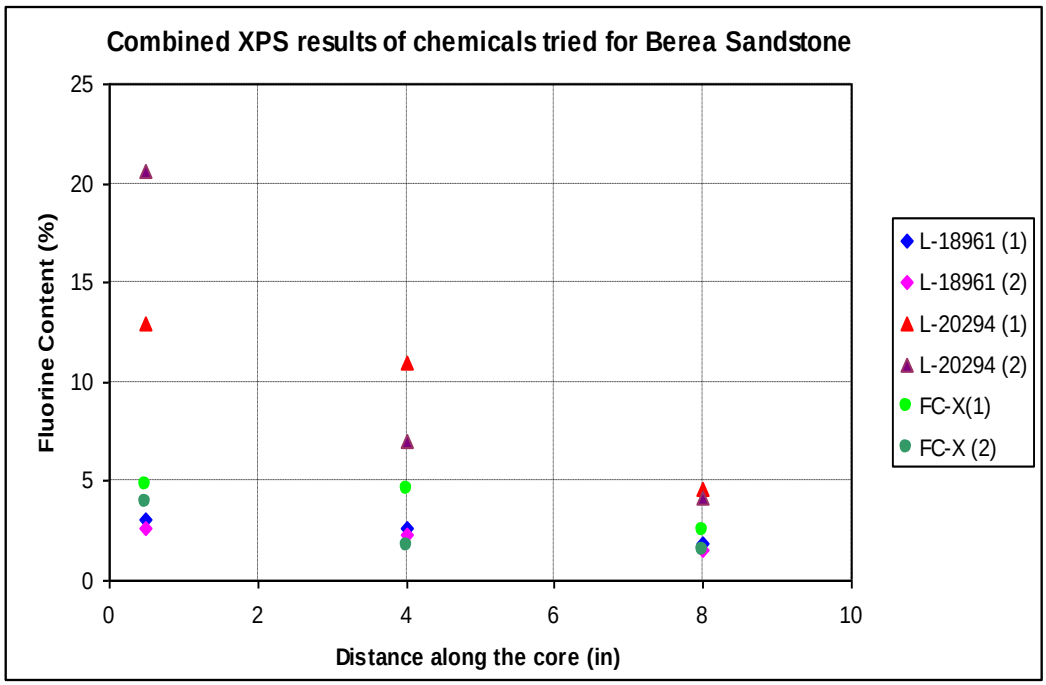

Figure 5.11: Plot of fluorine content versus distance along the core for all chemicals

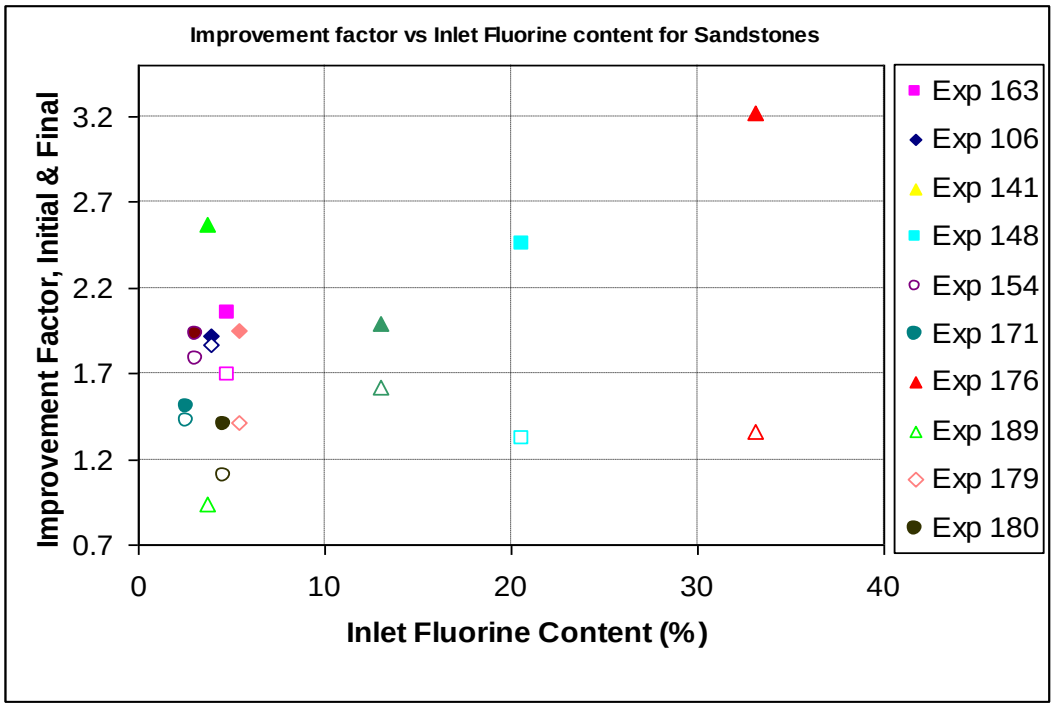

Figure 5.12: Plot of Improvement factor versus inlet fluorine content for all chemicals. The colored objects show initial IF; the empty objects show final IF

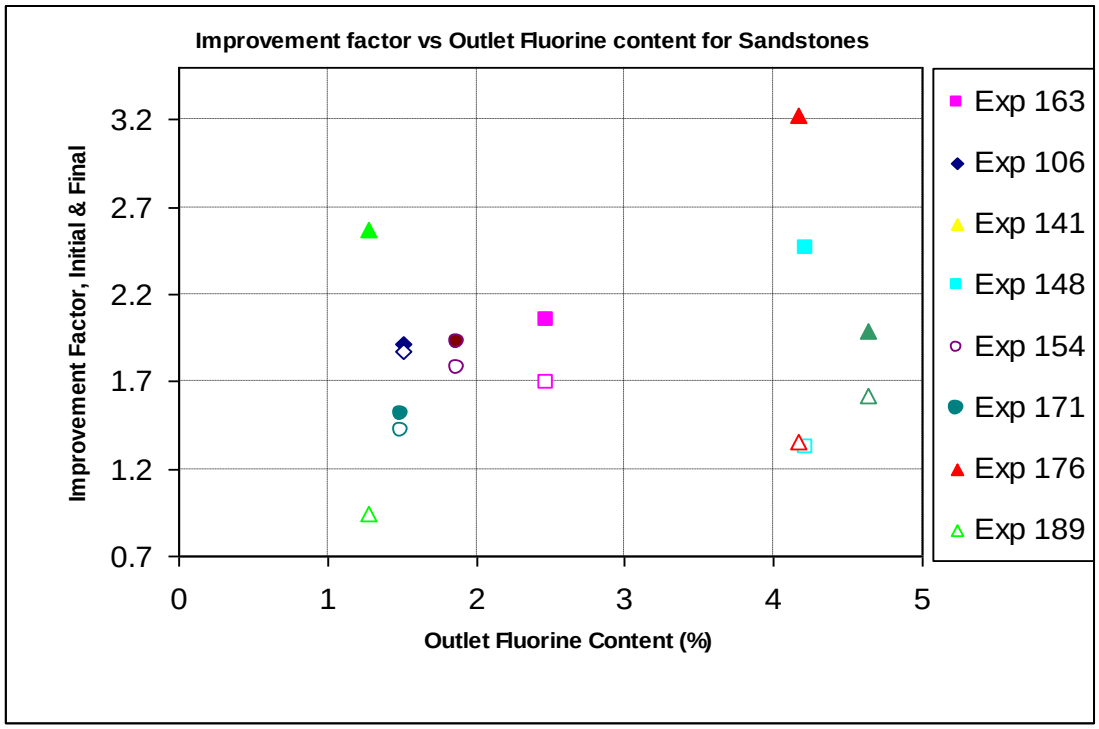

Figure 5.13: Plot of Improvement factor versus outlet fluorine content for all chemicals. The colored objects show initial IF; the empty objects show final IF

CHAPTER 6: RESULTS AND DISCUSSION FOR TEXAS CREAM LIMESTONE

In this chapter results are presented for XPS analysis, wettability tests and core floods (conducted by other members of the research group). A comparison between these measurements shows that the results are correlated under certain conditions allowing us to use simple drop tests or XPS analysis as screening tests for fluoro-carbon surfactants.

The methodology used was the same as mentioned in chapter 5 for sandstones. Following is a discussion of the results obtained for limestones

6.1 ANALYSIS FOR CHEMICAL L-18961

6.1.1 Stability/Compatibility Tests

The results for stability/compatibility tests for this chemical are already presented in the results section of sandstones.

6.1.2 Drop Tests

After observing satisfactory performance with Butoxy ethanol-Ethnaol as a solvent, drop tests were conducted on the treated rock chips to observe any wettability change. Drop tests were performed with decane and water being dropped on the treated chips and comparing their imbibition with untreated chips. As expected, decane and water imbibed readily onto the untreated chips. In the treated chips, however, decane imbibed into the sample in approximately thirty seconds where as water didn't imbibe at all for more than one minute. This suggests that the treatment has altered the wettability of the initially water-wet rock to neutral wet. Figure 6.1 shows the picture of drop test taken ten seconds after dropping water and decane on the treated chips.

6.1.3 XPS on Chips

The results for the XPS tests do show significantly higher fluorine content for the treated chips as compared to the untreated chips as shown in figure 6.2

6.1.4 Core Flood Results

After performing solubility tests, drop tests and XPS tests on chips, the chemical L-18961 with BE-Ethanol-IPA as solvents was used in two core flood experiments to observe its effectiveness. It was deemed to be a satisfactory chemical for limestone as it yielded improvement factors around 1.4. Table 6.1 lists the important details and results of the core flood experiments.

6.1.5 XPS results from treated core

After getting high improvement factors for both core flood experiments, the cores were tested for fluorine presence across the core. Chips were taken from the top, middle and bottom of the core and fluorine content was estimated using XPS analysis. Table 6.2 lists the fluorine content at three points; inlet, middle and outlet of the two cores. The core from experiment 169 showed marginally higher fluorine content than experiment 172 at the inlet of the core which explains the marginally higher improvement factor of 1.47. For both cores, a decreasing trend of fluorine concentration across the core was observed as shown in Figure 6.3.

6.2 ANALYSIS FOR CHEMICAL L-20294

6.2.1 Stability/Compatibility Tests

The results for stability/compatibility tests for this chemical are already presented in the results section of sandstones.

6.2.2 Drop Tests

After observing satisfactory performance with butoxy ethanol-ethnaol as a solvent, drop tests were conducted on the treated rock chips to observe any wettability change. As expected, decane and water imbibed readily onto the untreated chips. In the treated chips, however, decane imbibed into the sample in approximately forty seconds where as water didn't imbibe at all for more than one minute. This suggests that the treatment has altered the wettability of the initially water-wet rock to neutral wet. Figure 6.4 shows the picture of drop test taken forty seconds after dropping water and decane on the treated chips.

6.2.3 XPS on Chips

The results for the XPS tests do show significantly higher fluorine content for the treated chips as compared to the untreated chips as shown in figure 6.5.

6.2.4 Core Flood Results

After performing solubility tests, drop tests and XPS tests on chips, the chemical L-20294 with butoxy ethanol -ethanol as solvent was used in two core flood experiments to observe its effectiveness. The results were mixed i.e. the treatment showed high improvement factor in experiment 140 but failed to improve the gas relative permeability in experiment 165. Table 6.3 lists the important details and results of the core flood experiments.

6.2.5 XPS results from treated core

After getting mixed results from the core flood experiments, the cores were tested for fluorine presence across the core. Chips were taken from the top, middle and bottom of the core and fluorine content was estimated using XPS analysis. Table 6.4 lists the fluorine content at three points; inlet, middle and outlet of the two cores. Experiment 140 showed lower fluorine content across the core which explains for the lower improvement factor. It can be concluded that more surfactant had to be present across the core to bring about the desired wettability change. For both cores, a decreasing trend of fluorine concentration across the core was observed as shown in Figure 6.6.

6.3 ANALYSIS FOR CHEMICAL L-19446# 1

6.3.1 Stability/Compatibility Tests

For L-19446# 1, 2BE-EtOH-IPA (60-30-10) was used as a solvent at different temperatures since it had proved to be a good solvent as per our previous experiments. Table 6.5 shows the results of the conducted stability/solubility tests.

After performing the stability/solubility test, the treatment solution was tested for compatibility with brine. Different percentages of brine were added to treatment solution and tested at different temperatures. It was observed that this specific treatment solution remained clear at all temperatures up to a brine concentration of 50% so it was concluded that this chemical is perfectly compatible with the solvent used. Table 6.6 shows the results of the conducted compatibility tests.

6.3.2 Drop Tests

After observing satisfactory performance with 2BE-EtOH-IPA (60-30-10) as a solvent, drop tests were conducted on the treated rock chips to observe any wettability

change. As expected, decane and water imbibed readily onto the untreated chips. In the treated chips, however, decane imbibed quickly as compared to water. However, both the chips showed wettability change. This suggests that the treatment has altered the wettability of the initially water-wet rock to neutral wet. Figure 6.7 shows the picture of drop test taken forty seconds after dropping water and decane on the treated chips.

6.3.3 XPS on Chips

The results for the XPS tests do show significantly higher fluorine content for the treated chips as compared to the untreated chips as shown in figure 6.8.

6.3.4 Core Flood Results

After performing solubility tests, drop tests and XPS tests on chips, the chemical L-19446# 1 with butoxy ethanol -ethanol-IPA as solvent was used in four core flood experiments to observe its effectiveness. The results were favorable as the improvement factors varied from 2.17 to 1.38 for the four experiments. Table 6.7 lists the important details and results of the core flood experiments.

6.2.5 XPS results from treated core

After getting mixed results from the core flood experiments, the cores were tested for fluorine presence across the core. Table 6.8 lists the fluorine content at three points; inlet, middle and outlet of the two cores. The cores with lower fluorine content showed low improvement factors as expected. The results showed a decreasing trend of fluorine concentration across the core was observed as shown in Figure 6.9.

6.4 ANALYSIS FOR CHEMICAL L-19446# 2

6.4.1 Stability/Compatibility Tests

For L-19446# 2, 2BE-EtOH-IPA (60-30-10) was used as a solvent at different temperatures since it had proved to be a good solvent as per our previous experiments. Table 6.9 shows the results of the conducted stability/solubility tests.

After performing the stability/solubility test, the treatment solution was tested for compatibility with brine. Different percentages of brine were added to treatment solution and tested at different temperatures. It was observed that this specific treatment solution remained clear at all temperatures up to a brine concentration of 50% so it was concluded that this chemical is perfectly compatible with the solvent used. Table 6.10 shows the results of the conducted compatibility tests.

6.4.2 Drop Tests

After observing satisfactory performance with 2BE-EtOH-IPA (60-30-10) as a solvent, drop tests were conducted on the treated rock chips to observe any wettability change. As expected, decane and water imbibed readily onto the untreated chips. In the treated chips decane imbibed quickly while water didn't imbibe at all for more than one minute. This suggests that the treatment has altered the wettability of the initially water-wet rock to neutral wet. Figure 6.10 shows the picture of drop test taken forty seconds after dropping water and decane on the treated chips.

6.4.3 XPS on Chips

The results for the XPS tests do show significantly higher fluorine content for the treated chips as compared to the untreated chips as shown in figure 6.11.

6.4.4 Core Flood Results

After performing solubility tests, drop tests and XPS tests on chips, the chemical L-19446# 2 with BE-Ethanol-IPA as solvent was used in two core flood experiments to observe its effectiveness. The results were favorable as the improvement factors varied from 1.95 to 1.4 for the two experiments. Table 6.11 lists the important details and results of the core flood experiments.

6.4.5 XPS results from treated core

Table 6.12 lists the fluorine content at three points; inlet, middle and outlet of the two cores. The cores with lower fluorine content showed low improvement factors as expected. The results showed a decreasing trend of fluorine concentration across the core was observed as shown in Figure 6.12.

A plot containing all the XPS results conducted on limestone cores is given in Fig 6.13. Fig 6.14 & 6.15 show the trend of improvement factor versus inlet & outlet fluorine content for Limestones.

Table 6.1: Core flood results with chemical L-18961 in 2BE-EtOH-IPA (60-30-10)

	Experiment 169	**Experiment 172**
K, md	5.92	16
Temperature, ^{o}F	175	230
Chemical	L-18961	L-18961
Solvent	2BE-EtOH-IPA (60,30,10)	2BE-EtOH-IPA (60,30,10)
Nc	1.66E-06	3.62E-06
Initial Krg	0.111	0.117
Improvement Factor	1.47-1.29	1.43-1.21

Table 6.2: Amount of fluorine present with distance along the core (XPS test)

Distance along the core	**Fluorine Content**	
	Experiment 169	**Experiment 172**
0.5	19.12	18.31
4	15.29	14.24
8	10.79	9.77
IF	1.47-1.29	1.43-1.21

Table 6.3: Core flood results with chemical L-20294 in 2BE-EtOH (70-30)

	Experiment 140	**Experiment 165**
K, md	19.6	4.6
Temperature, ^{o}F	175	175
Chemical	L-20294	L-20294
Solvent	2 BE-EtOH(70-30)	2 BE-EtOH(70-30)
Nc	3.73E-06	1.53E-06
Initial Krg	0.095	0.121
Improvement Factor	1.76-1.42	1.06-0.86

Table 6.4: Amount of fluorine present with distance along the core (XPS test)

Distance along the core	**Fluorine Content**	
	Experiment 140	**Experiment 165**
0.5	7.85	4.87
4	4.46	2.28
8	0.12	0.07
IF	1.76-1.42	1.06-0.86

Table 6.5: Stability data for chemical L-19446 #1

Chemical Conc., %	Solvent	Room Temperature	175 °F	250 °F
1	2BE-EtOH-IPA (60-30-10)	Clear	Clear	Clear
2	2BE-EtOH-IPA (60-30-10)	Clear	Clear	Clear

Table 6.6: Compatibility data for 2% L-19446#1 in 2BE-EtOH (70-30)

Brine Mass%	Room Temperature	175 °F
20	Clear	Clear
25	Clear	Clear
30	Clear	Clear
35	Clear	Clear
40	Clear	Clear
45	Clear	Clear
50	Clear	Clear

Table 6.7: Core flood results with chemical L-19446# 1 in 2BE-EtOH-IPA (60-30-10)

	Exp# 182	Exp# 184	Exp# 185	Exp# 188
K, md	11.3	24.6	24.8	20.4
Temperature, ^{o}F	175	175	155	175
Chemical	L-19446# 1	L-19446# 1	L-19446# 1	L-19446# 1
Solvent	2BE-EtOH-IPA (60-30-10)	2BE-EtOH-IPA (60-30-10)	2BE-EtOH-IPA (60-30-10)	2BE-EtOH-IPA (60-30-10)
Nc	1.78E-06	1.97E-06	1.67E-06	1.76E-06
Initial Krg	0.106	0.058	0.065	0.108
Improvement Factor	2.11-1.33	2.17-1.84	1.82-1.73	1.38-1.13

Table 6.8: Amount of fluorine present with distance along the core (XPS test)

Distance along the core	**Fluorine Content**			
	Experiment 182	**Experiment 184**	**Experiment 185**	**Experiment 188**
0.5	14.11	15.76	19.54	10.08
4	6.36	10.78	9.93	5.03
8	3.61	2.61	4.68	1.64
IF	2.11-1.33	2.17-1.84	1.82-1.73	1.38-1.13

Table 6.9: Stability data for chemical L-19446 # 2

Chemical Conc., %	Solvent	Room Temperature	175 °F	250 °F
1	2BE-EtOH-IPA (60-30-10)	Clear	Clear	Clear
2	2BE-EtOH-IPA (60-30-10)	Clear	Clear	Clear

Table 6.10: Compatibility data for 2% L-19446# 2 in 2BE-EtOH-IPA (60-30-10)

Brine Mass%	Room Temperature	175 °F
20	Clear	Clear
25	Clear	Clear
30	Clear	Clear
35	Clear	Clear
40	Clear	Clear
45	Clear	Clear
50	Clear	Clear

Table 6.11: Core flood results with chemical L-19446# 2 in 2BE-EtOH-IPA (60-30-10)

	Experiment 179	**Experiment 180**
K, md	12.6	23.6
Temperature, ^{o}F	175	175
Chemical	L-19446 #2	L-19446 #2
Solvent	2BE-EtOH-IPA (60-30-10)	2BE-EtOH-IPA (60-30-10)
Nc	4.35E-06	4.6E-06
Initial Krg	0.087	0.082
Improvement Factor	1.95-1.41	1.4-1.1

Table 6.12: Amount of fluorine present with distance along the core (XPS test)

Distance along the core	**Fluorine Content**	
	Experiment 179	**Experiment 180**
0.5	17.58	15.2
4	7.4	6.89
8	5.37	4.61
IF	1.95-1.41	1.4-1.1

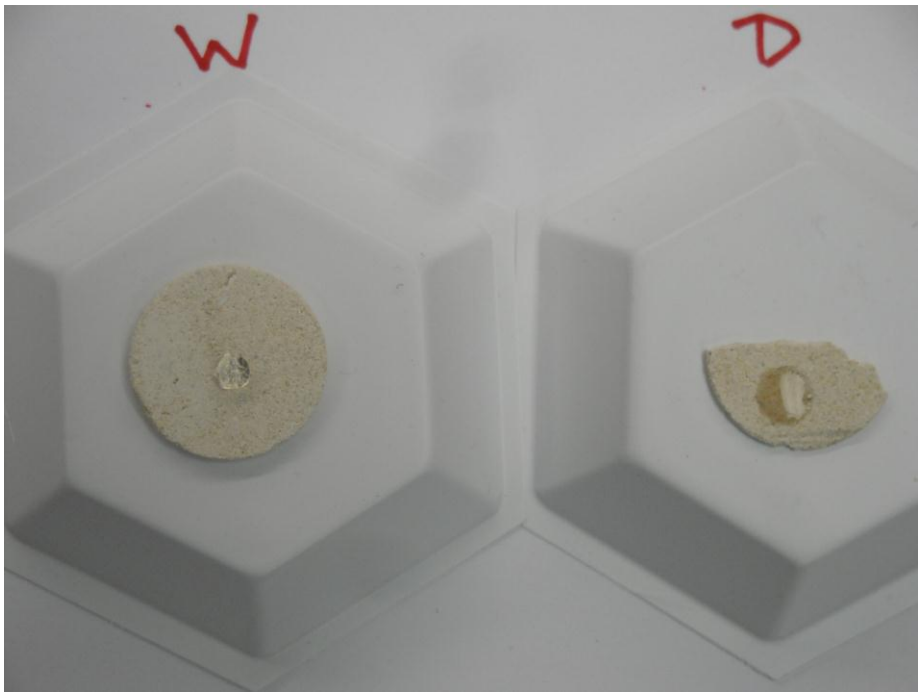

Figure 6.1: Drop tests on sandstone chips treated with L-18961. 'W' denotes water drop and 'D' denotes decane drop.

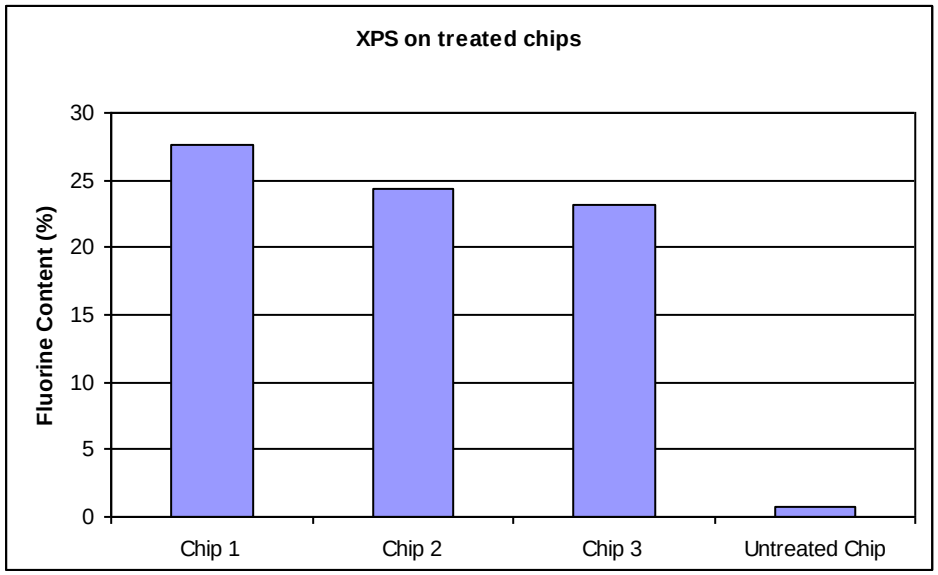

Figure 6.2: Fluorine content on sandstone chips treated with L-18961 (XPS tests)

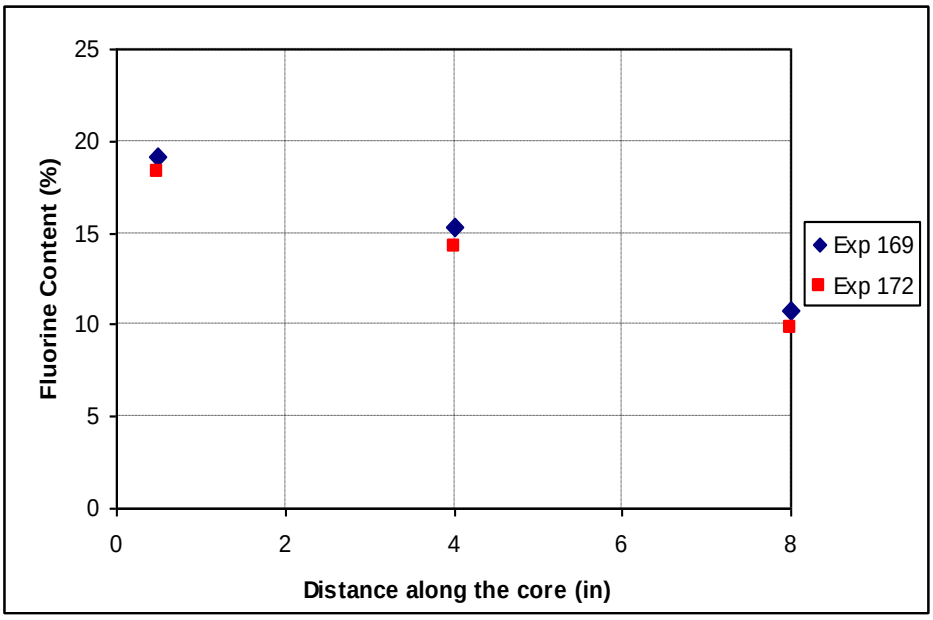

Figure 6.3: Plot of fluorine content versus distance along the core for different experiments with L-18961

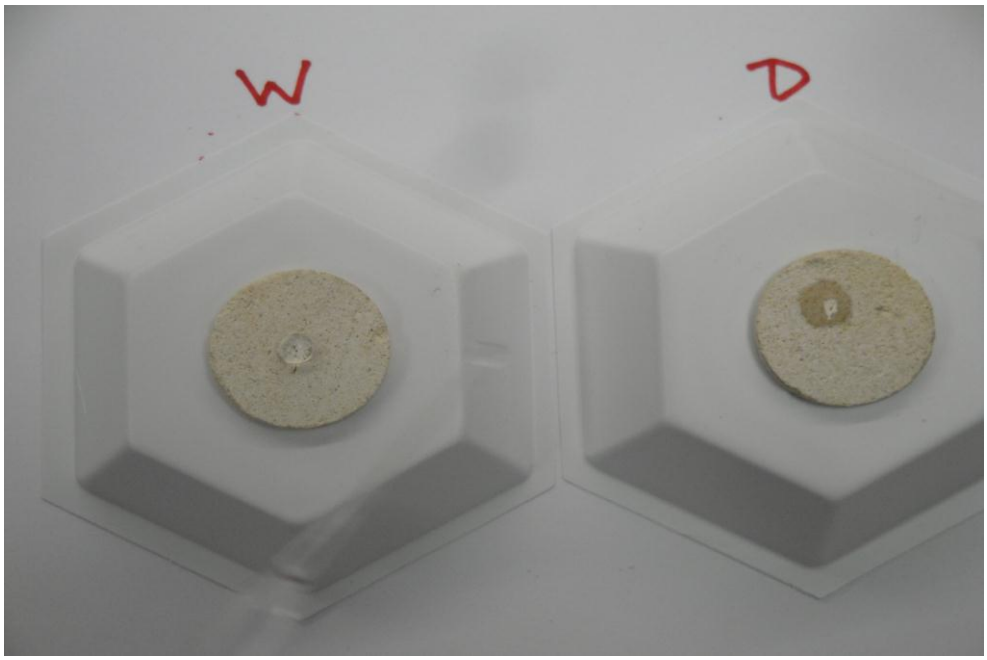

Figure 6.4: Drop tests on sandstone chips treated with L-20294. 'W' denotes water drop and 'D' denotes decane drop.

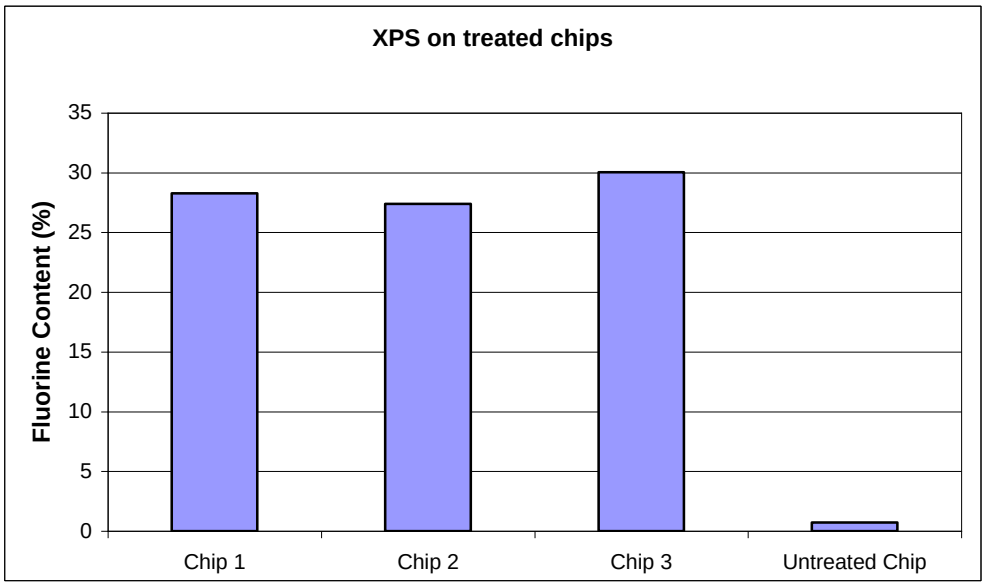

Figure 6.5: Fluorine content on sandstone chips treated with L-20294 (XPS tests)

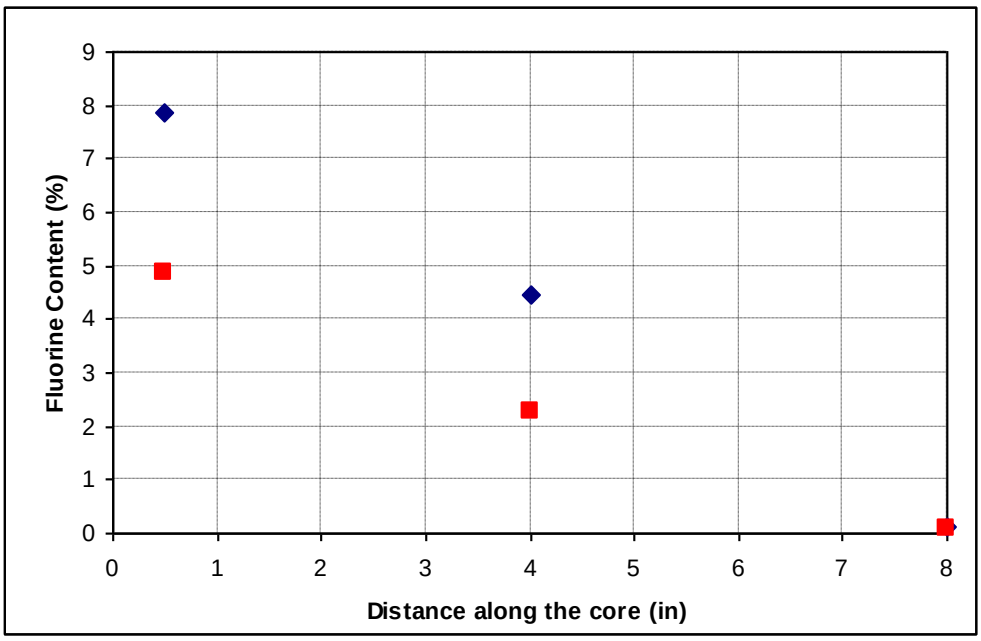

Figure 6.6: Plot of fluorine content versus distance along the core for different experiments with L-20294

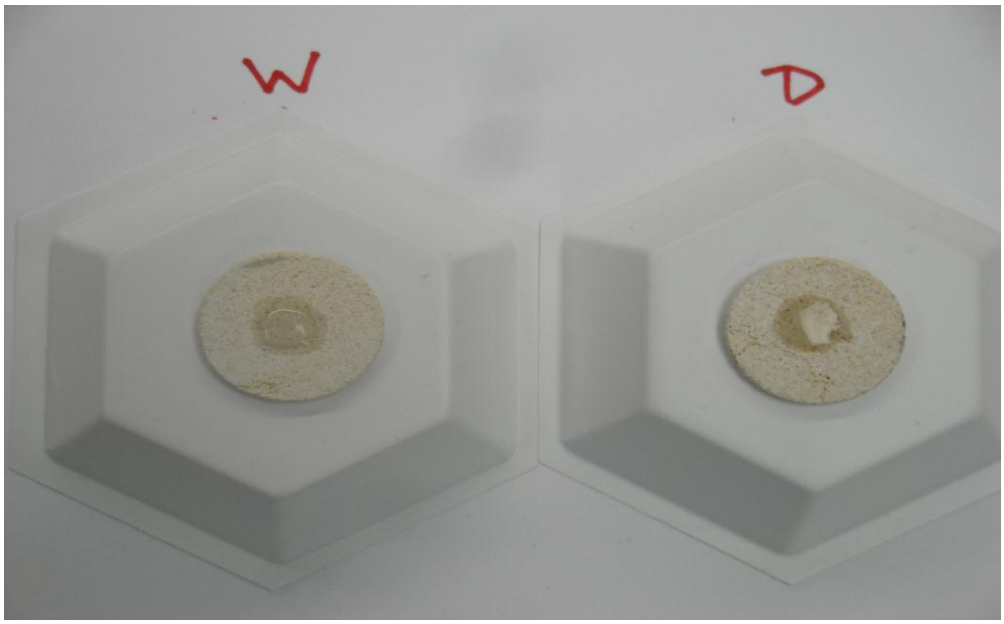

Figure 6.7: Drop tests on sandstone chips treated with L-19446# 1. 'W' denotes water drop and 'D' denotes decane drop

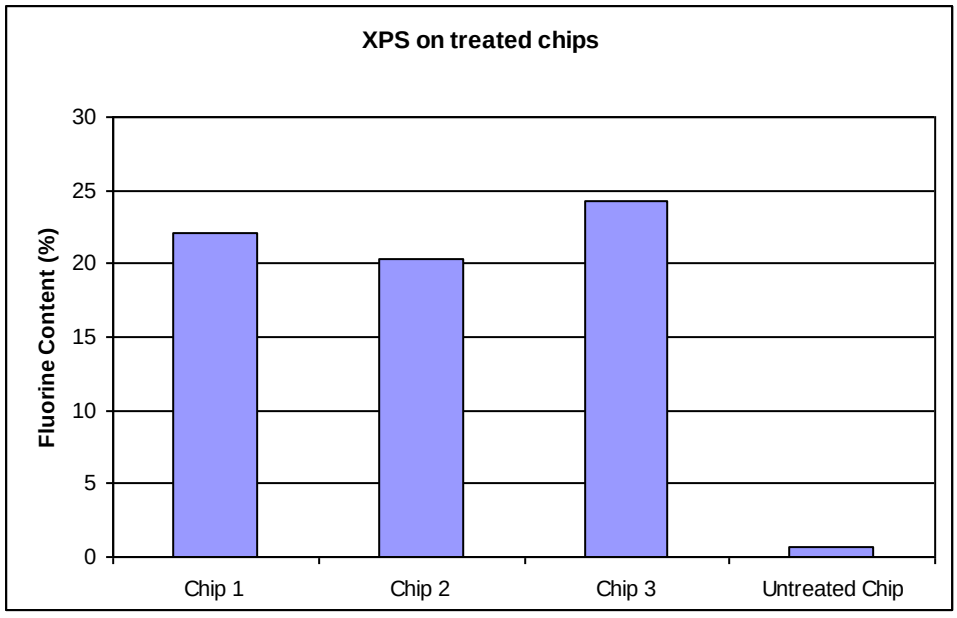

Figure 6.8: Fluorine content on sandstone chips treated with L-19446# 1 (XPS tests)

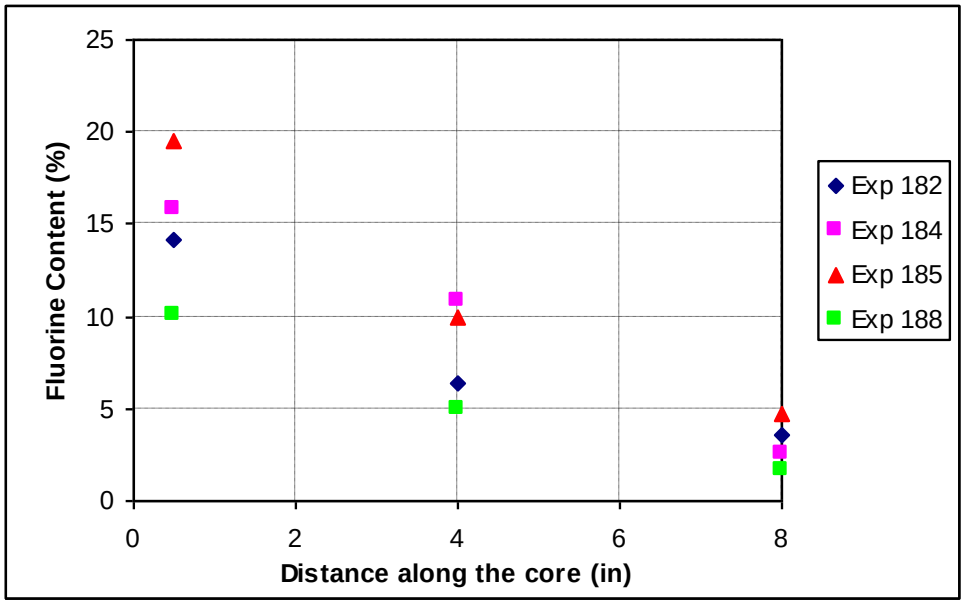

Figure 6.9: Plot of fluorine content versus distance along the core for different experiments with L-19446# 1

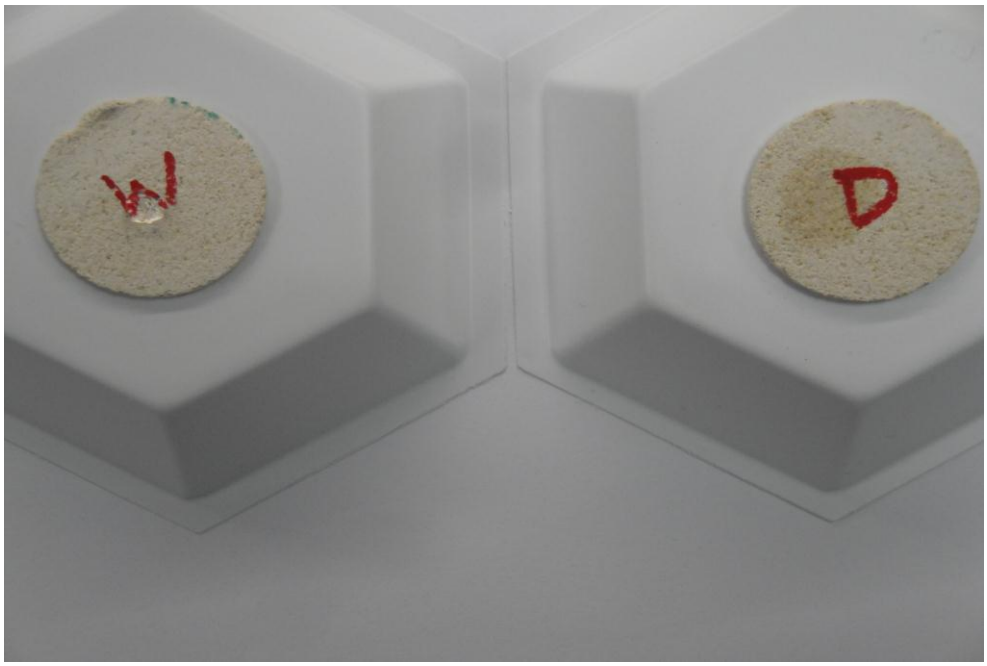

Figure 6.10: Drop tests on sandstone chips treated with L-19446# 2. 'W' denotes water drop and 'D' denotes decane drop

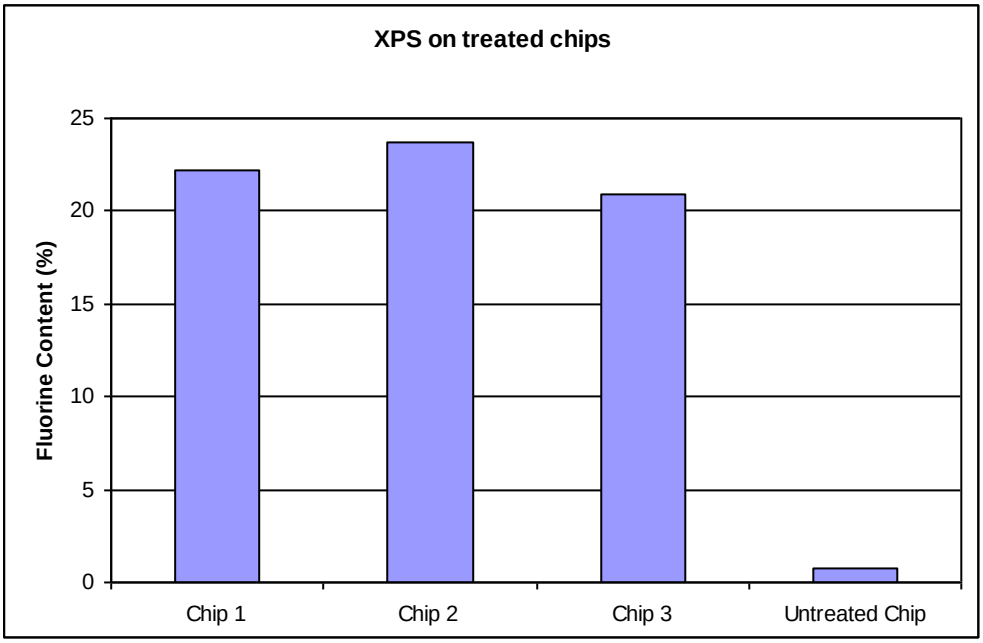

Figure 6.11: Fluorine content on sandstone chips treated with L-19446# 2 (XPS tests)

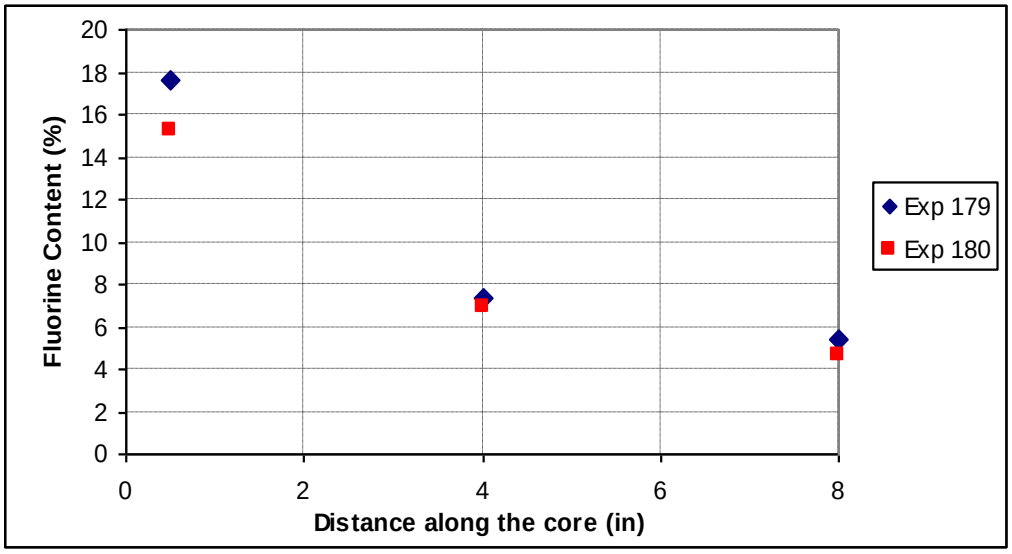

Figure 6.12: Plot of fluorine content versus distance along the core for different experiments with L-19446# 2

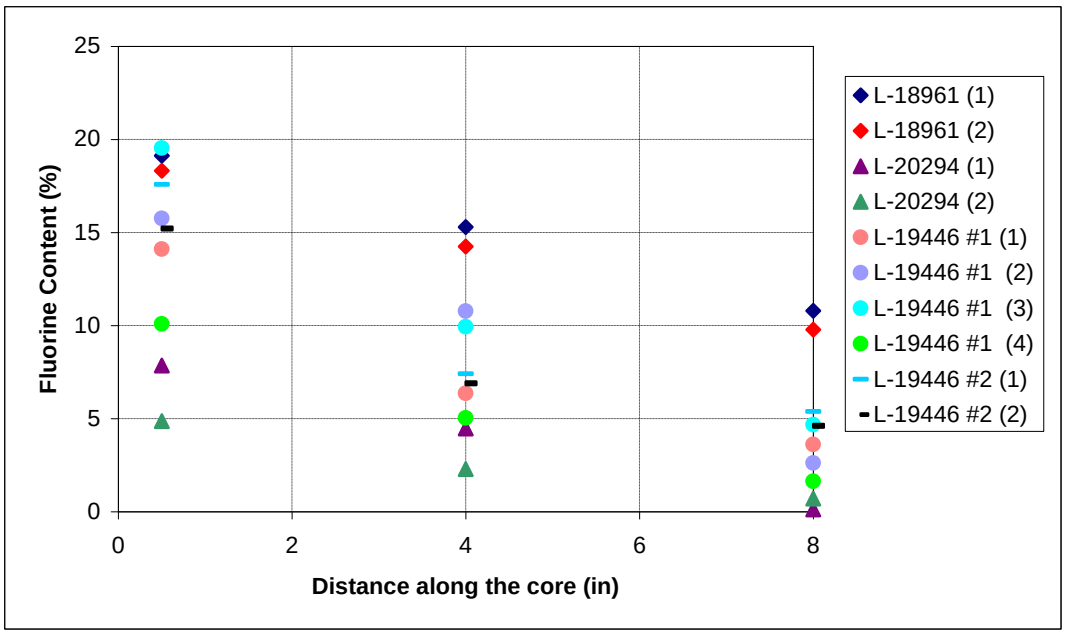

Figure 6.13: Plot of fluorine content versus distance along the core for all chemicals

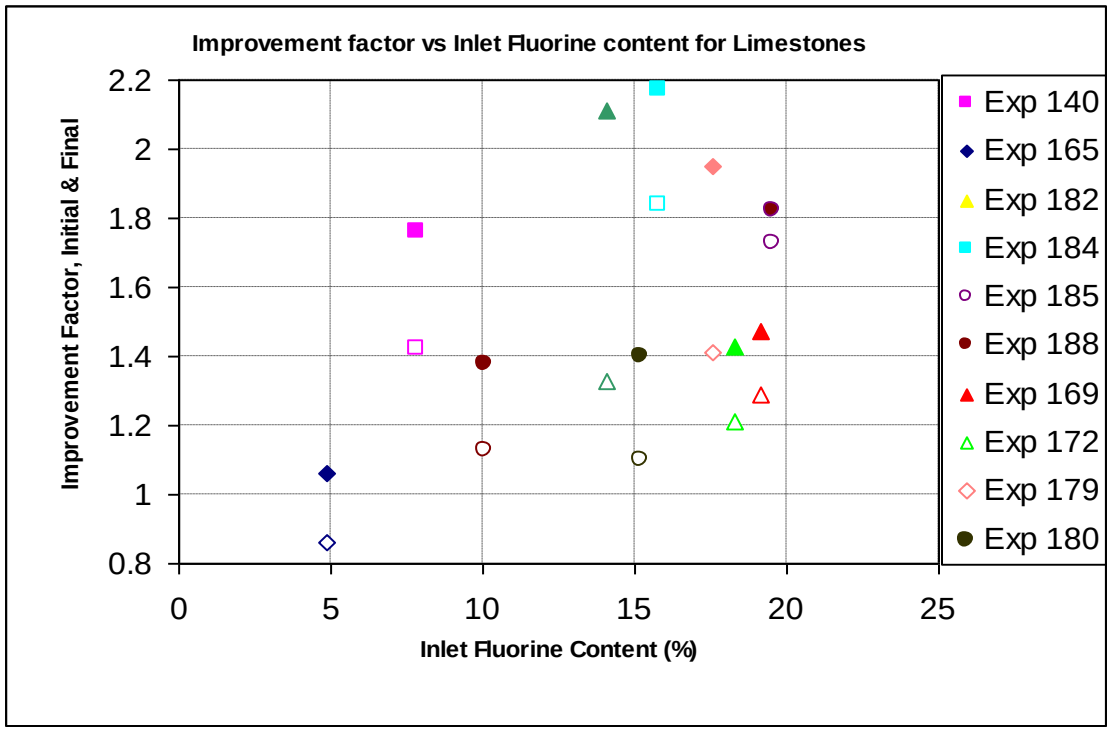

Figure 6.14: Plot of Improvement factor versus inlet fluorine content for all chemicals. The colored objects show initial IF; the empty objects show final IF

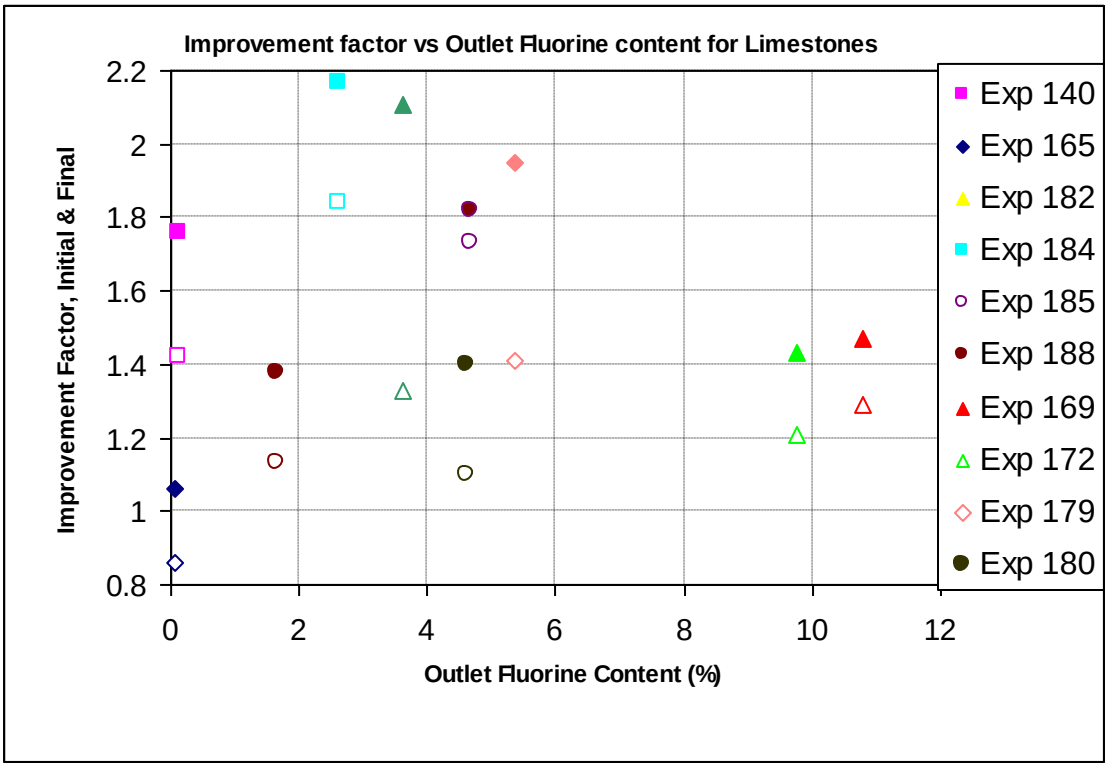

Figure 6.15: Plot of Improvement factor versus outlet fluorine content for all chemicals. The colored objects show initial IF; the empty objects show final IF

Chapter 7: Conclusions and Recommendations for Future Work

Screening tests were developed and evaluated to aid in the selection of treatment chemicals and solvents to be used for chemical treatment of condensate blocking. Based on the results presented in this research, the following screening tests are recommended:

1. Measure the cloud point of non-ionic surfactants. The solvent should be designed so that the cloud point temperature is higher than the reservoir temperature. The surfactant does not adsorb on the rock if the interaction between the solvent and the surfactant is too strong, which means the cloud point should not be too much lower than the reservoir temperature.

2. Compatibility tests to choose treatment solutions that are stable under reservoir conditions of temperature and salinity.

3. Drop tests on untreated and treated rock chips to visually determine wettability alteration.

4. X-ray photoelectron spectroscopy (XPS) to determine the fluorine content before and after the treatment. A positive but imperfect correlation between improvement factor and fluorine content was observed. It was observed that there is a decreasing trend of fluorine concentration on the surface of the rock from the inlet to the outlet of the core for almost all experiments. Possible reasons could be

- All the adsorption sites have not been covered with the surfactant.
- The surfactant is desorbing from the outlet of the core.

The complete set of screening tests evaluated in this thesis together with core flood experiments helps to quickly identify suitable treatment solutions for sandstone and limestone reservoirs. Such screening tests save time, effort and money.

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